EGE UNIVERSITY GRADUATE SCHOOL OF APPLIED AND
NATURAL SCIENCES
(MASTER OF SCIENCE THESIS)

NEW METHACRYLIC BASED COPOLYMER SYNTHESIS FOR COATING INDUSTRY

Volkan Özenç

Chemical Engineering
603.01.00

September, 2009

Supervisor : Prof. Dr. Mesut YENİGÜL

Bornova, Izmir

Volkan ÖZENÇ tarafından **Yüksel Lisans** tezi olarak sunulan **“New Methacrylic Based Copolymer for Coating Industry**” başlıklı bu çalışma, E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliği ile E.Ü. Fen Bilimleri Enstitü Eğitim ve Öğretim Yönergesi’nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve **03.09.2009** tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

		İmza
Jüri Başkanı	: Prof. Dr. Mesut YENİGÜL	....
Raportör Üye	: Prof. Dr. Sevgi ULUTAN	....
Üye	: Prof. Dr. Mehmet BALCAN	…………………….

ÖZET

KAPLAMA ENDÜSTRİSİ İÇİN METAKRİLİK BAZLI YENİ BİR KOPOLİMER SENTEZİ

ÖZENÇ, Volkan

Yüksek Lisans Tezi, Kimya Mühendisliği Bölümü
Tez Yöneticisi: Prof. Dr. Mesut YENİGÜL
Eylül, 2009, 63 sayfa

Bu çalışmanın amacı, kısa yağlı alkid ile uyumlu Metil Metakrilat ve i.BMA kopolimerlerinin laboratuar ölçeğinde hazırlanmasıdır. Bu amaç için, farklı monomer besleme oranlarında yapılan süspansiyon polimerizasyonlarından elde edilen akrilik kopolimerlerin alkid ile uyumluluk testleri Ubbelohde viskometresi kullanılarak yapılmıştır. Sonuçlar gösteriyor ki; i.BMA monomerinin kopolimer içindeki fraksiyonu ile kopolimerin alkid ile uyumluluğu arasında bir bağlantı yoktur. i-BMA monomerinin kopolimer içindeki fraksiyonu ile kopolimerin camsı geçiş sıcaklığı arasında ters orantılıdır bir ilişki olduğu gözlenmiştir.

Kopolimer molekül ağırlığının uyumluluk üzerindeki etkisini ortaya çıkarmak için zincir transfer ajanı kullanılarak farklı molekül ağırlıklarında kopolimer sentezlenmiştir. Zincir transfer ajanı olarak Benzil merkaptan kullanılmış ve 0,099 dl/g intrinsik viskozite değerine sahip kopolimer #7 elde edilmiştir. 0,762 dl/g intrinsik viskozite değerine sahip olan kopolimer #4 ile kopolimer #7 kıyaslandığı, Flory-Huggins teorisinin ortaya koyduğu gibi molekül ağırlığı düşüşüyle beraber karışımın entropisi artmaktadır. Bu artış, Gibbs serbest enerjisinin negatif değer almasını ve uyumluluğun gözlemlenmesini sağlamaktadır. Kopolimer #4, kopolimer/alkid oranı 20/80 ve 40/60 durumda kısa yağlı alkid ile uyumlu olarak gözlenmiş ve faz ayırımı olmamıştır. Kopolimer#7 ise 20/80, 40/60 ve 60/40 kopolimer/alkid oranlarında uyumlu olduğu gözlemlenmiştir.

Anahtar Sözcükler: Akrilik kopolimer, Alkid, Polimer/Polimer uyumluluğu, MMA, i-BMA.

ABSTRACT

NEW METHACRYLIC BASED COPOLYMER SYNTHESIS FOR COATING INDUSTRY

ÖZENÇ, Volkan

Master of Science Thesis, Department of Chemical Engineering
Supervisor: Prof**.** Dr. Mesut YENİGÜL
September, 2009, 63 pages

The aim of this study is laboratory scale preparation of MMA and i.BMA copoylmers compatible with short oil alkyds. For this aim, copolymers which had different monomer feed ratio is produced by suspension polymerization. Viscometric investigation of compatibility was done by Ubbelohde viscometer. The results show that there no relationship between compatibility and monomer fraction of i-BMA in the acrylic copolymer of MMA and i-BMA. Glass transition temperature of the copolymer is inversely related to molar fraction of i-BMA in the copolymer.

To show the relation between molecular weight of copolymer and compatibility, different molecular weight copolymers were produced by chain transfer mechanism. Benzyl mercaptan was used as transfer agent and Copolymer Run#7 was obtained with intrinsic viscosity value of 0,099. Copolymer Run#4 with intrinsic viscosity value of 0,762 was compared with Copolymer Run#7. As the Flory-Huggins theory points out, the entropy gain on mixing of copolymers which have low molecular weights increases. This increase provides negative value of the Gibbs free energy, so miscibility has occurred. Copolymer/Alkyd weight ratios for compatible mixtures are 20/80 and 40/60 for Copolymer Run#4. These ratios for Copolymer Run#7 are 20/80, 40/60 and 60/40.

Key words: Acrylic copolymers, Alkyd, Compatibility, MMA, i-BMA.

ACKNOWLEDGEMENT

I would like to thank my supervisor, Prof**.** Dr. Mesut YENİGÜL for suggesting me to investigate such an interesting and necessary subject. I am deeply indebted to him for valuable suggestions and encouragement that helped me during the time of research, experimental study and writing of this thesis.

I would like to thank Research Deparmant of Akzo Nobel Kemipol A.S., for giving me support to do the necessary research work. and to use deparmental data.

I would like to give my special thanks to my family, whose patience and support enabled me to complete this work

Volkan Özenç, September 2009, Bornova

TABLE OF CONTENTS

LIST OF FIGURES

Figure **Page**

LIST OF TABLES

Table **Page**

NOMENCLATURE

$k_{1,2}$: Kinetic rate constants

F : Mole fraction of monomer in the increment of polymer

f : Mole fraction of unreacted monomer

$r_{1,2}$: Reactivity ratios

Mn : molecular weight

C : Chain Transfer constant

R : The gas constant

χ_{AB} : The Flory–Huggins interaction parameter

ϕ_i : Volume fraction

δ_i : Solubility parameters

$[\eta]$: Intrinsic viscosity (dl/g)

η_{sp} : Specific viscosity

1. INTRODUCTION

Materials that form the continuous film are binders. They adhere to the surface being coated. In the coating, other substances are bonded together to form a film for an adequately hard outer surface [1].

A variety of polymers are used in coatings. Acrylics are the big role players in industrial applications. Since their introduction, acrylics are gained importance in the coatings as a result of improved flexibility, adhesion, outdoor durability, resistance to ultraviolet degradation. Using acrylic copolymers in the alkyd blends improves dry-time, film clarity, gloss retention and outdoor durability.

The aim of this study is laboratory scale preparation of a new acrylic copolymer compatible with alkyd resins.

1.1 Alkyds

Alkyd resin is a class of polymers that are used in surface coating formulations. Their advantages are low cost and versatility. The term “alkyd” is derived from “al” of alcohol and “cid” of acid; “cid” was later changed to ”kyd” [2].

However alkyds are no longer largest binders in coatings, alkyds are still of major importance. $410 million worth of alkyds were used in U.S. coatings in 2002. Alkyds are polyester product of reactions of polyols, dibasic acids, and fatty acids [1].

The main acid ingredient in an alkyd is phthalic acid or its anhydride, and the main alcohol is usually glycerol [3].

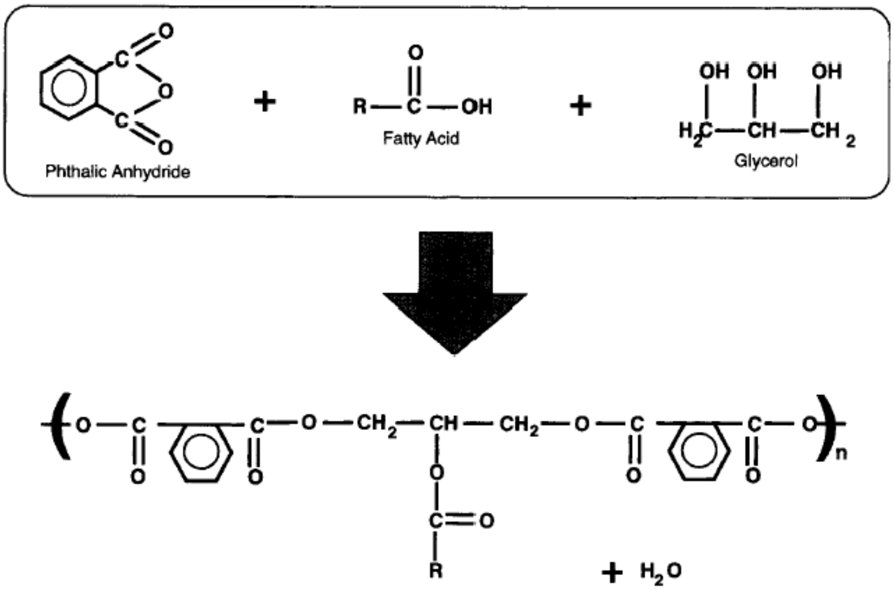


Figure 1.1: The structure of a typical alkyd resin [4].

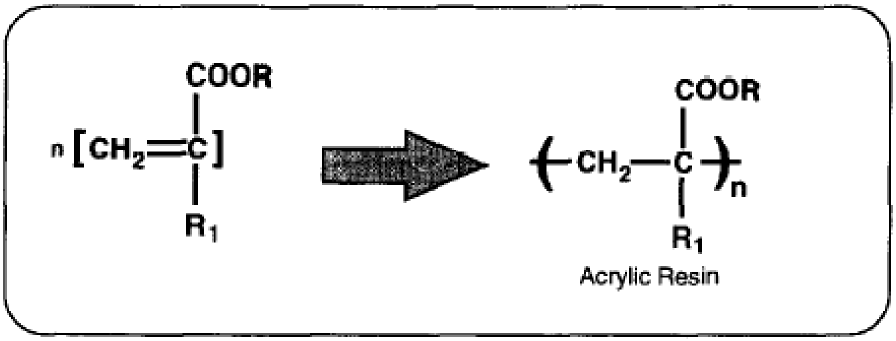
Alkyds are named as short oil (<%45), medium oil (45 to 55%), or long oil (>55%) depending on the weight percentage of fatty acid in the resin.

Long oil alkyds can be applied by brush and be used for exterior trim paints and wall paints, marine and metal maintenance paints. Another widely is clear lacquers. They are soluble in aliphatic solvents. The air drying type medium oil alkyds used as the standard vehicle of industrial application, such as primers, maintenance paints, and metal finishes. The non-oxidizing type is often used as external plasticizer in nitrocellulose lacquers. Short oil alkyds of the air drying type are used in baking primers and enamels, either as the sole binder or together with other resin (urea or melamine resins) and they are soluble in aromatic solvents. As the same use of medium oil alkyds, short oil alkyds of the nondrying type are used as plasticizing resin in nitrocellulose lacquers and in combination with urea or melamine resin in stoving and acid curing finish [2].

1.2 Acrylics

Acrylics are high performance level in polymer system. They are esters of methacrylic and acrylic acids such as methyl, ethyl, isobutyl, n-butyl, 2-ethylexyl, octyl, lauryl, and stearyl [2].

Figure 1.2 shows typical acrylic resins which are prepared though polymerization for acrylic and methacrylic acids or their corresponding ester. Acrylic resins are used as both a thermoplastic and thermoset polymers. Through solvent evaporation thermoplastic acrylic resins form hardened coatings. With a chemical reaction thermoset resins form a cross linked structure. This reaction can occur with itself or various other types of resins [2].



Where,

$R = H$; $R_1 = H$ Poly(acrylate)

$R = H$; $R_1 = CH_3$ Poly(methacrylate)

$R = CH_3$; $R_1 = CH_3$ Poly(methyl methacrylate)

Figure 1.2: Polymerization reactions for typical acrylic resins [2].

2. PRESENT STUDY

Garcia et al., (1999) studied the viscosity behaviour of mixtures by two uncharged polymers in dilute solution. Polymers were denoted as poly (ether sulphone) (PES) as polymer 1, and poly (vinlidene fluoride) (PVDF), poly(methyl methacrylate) (PMMA) or poly(styrene) (PS) as polymer 2. The estimation of the compatibility degree of the above polymer pairs had been done by means of three criteria: (i) the sign of Δb_m, according to the traditional formalism developed by Krigbaum and Wall; (ii) the sign of a new defined $\Delta b'_m$; and (iii) the sign of $\Delta[\eta]_m$. They concluded that: the advantage of the last two criteria ($\Delta b'_m$ and $\Delta[\eta]_m$) lies in the fact that it is not necessary to arbitrarily define the b_{12}^{id} parameter (either as geometric or as an arithmetic mean value) and that the calculations are much more simple, and only need the primary data obtained with respective binary polymer/solvent systems [5].

Baysal et al., (2006) studied the viscosity behaviour of poly(2,6-dimethyl-1,4-penylene oxide) (PPO), brominated polystyrene (PBrS) and their blends at several compositions (25/75, 50/50, 75/25, 85/15). The compatibility was investigated on the basis of the sign of the criteria Δb, α, ΔK, μ, and $\Delta[\eta]$ determined by viscosity. They concluded that: Δb, $\Delta b'$, and $\Delta[\eta]$ parameters as shown in Figure 2.1, succeed in predicting the miscibility of polymer blend of (PPO/PBrS), and implying that it is suitable to determine polymer-polymer miscibility [6].

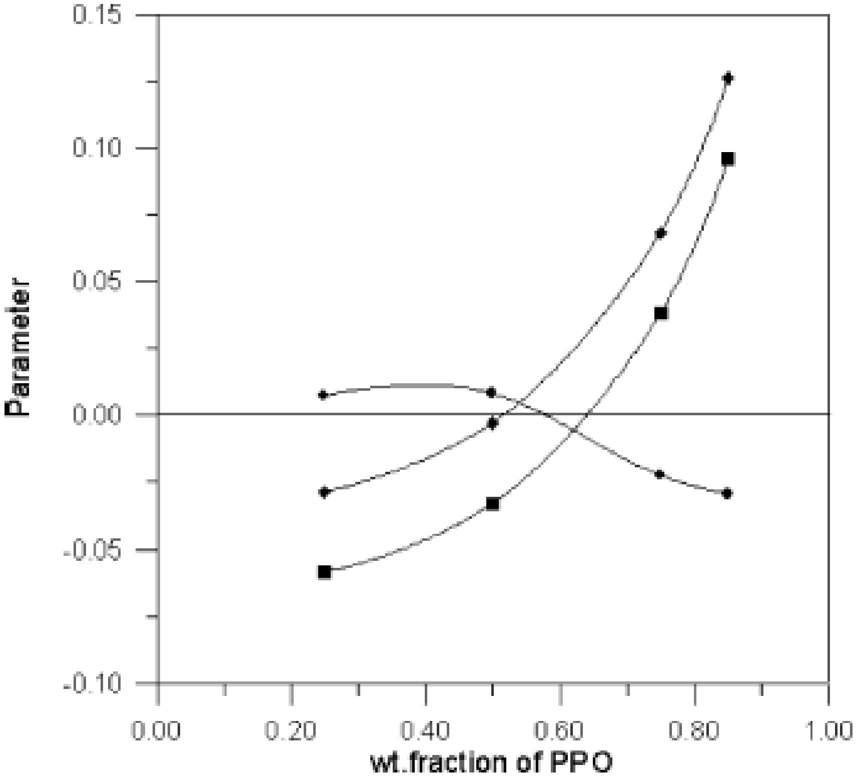


Figure 2.1: Miscibility parameters as a function of weight fraction of PPO (●) $\Delta[\eta]$, (♦) Δb, and (■) $\Delta b'$ [6].

Wanchoo et al., (2003) studied distilled water/sodium carboxymethylcellulose / polyacrylamide, distilled water / methylcellulose / carboxymethylcellulose and distilled water / polyvinylpyrrolidone polymer mixtures. They determined the intrinsic viscosities and viscometric interaction parameters for binary (distilled water/polymer) and ternary (distilled water/polymer1/polymer2) systems as shown in Figure 2.2 [7].

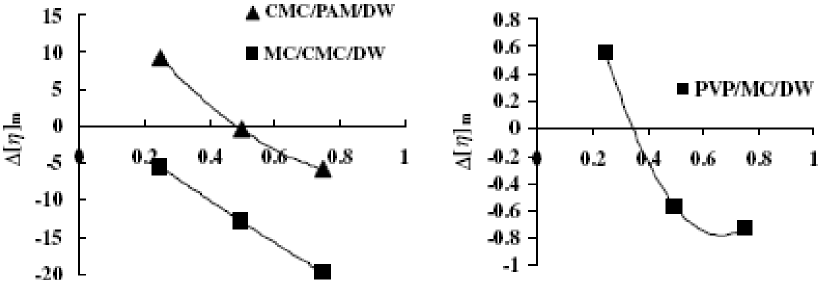


Figure 2.2: Plot of the criterion of $\Delta[\eta]_m$ vs. weight fraction of CMC/PAM/DW, MC/CMC/DW and PVP/MC/DW [7].

They concluded that inexpensive viscometric method can be used to within a fairly good accuracy in acquiring the compatibility of two polymers in solutions.

Pingping, (1997) employed an Ubbelohde dilution viscometer for measuring the relative viscosity of the polymer solutions in benzene at 25°C. Polystyrene, poly (methyl methacrylate) and poly (butadiene) was used for compatibility tests. Measured weights of polymers were diluted in benzene and then diluted in measured volumes. The intercept $[\eta]$ and slope b_m of plots of η_{sp}/c vs. c were obtained and used for compatibility criteria. These criteria were in good agreement with results in literature [8].

Aroguz et al., (2007) investigated polystyrene / brominated polystyrene blends by using dilute solution viscometry method. For prepared several PS / PBrS compositions (85/15, 75/25, 50/50, 25/75, 10/90) the intrinsic viscosity and viscometric parameters were determined at 20°C [9].

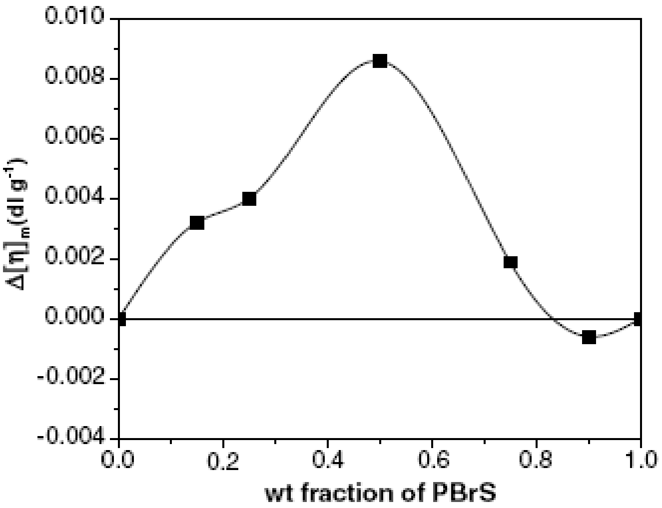


Figure 2.3: Plot of the criterion of $\Delta[\eta]_m$ vs weight fraction of PBrS in the PS/PBrS blend [9].

As shown in Figure 2.3, examined blends were immiscible in all compositions range besides the composition (10/90). DSC curve of PS / PBrS blend composition (10/90) showed single T_g. At the rest of the compositions, two glass transitions were obtained due to existence of two immiscible homopolymers and phase separation. The agreement on the results of the viscosity measurements and the thermal analysis for PS/PBrS system supported the validity of viscometric study[9].

Chee, (1990) studied poly (vinyl chloride), poly (methyl methacrylate) and poly (isobutyl methacrylate) for compatibility. He used method derived from the classical Huggins equation and that rested validity of an additivity law pertaining to intrinsic viscosity. It was found that PVC was miscible with PMMA and immiscible with PiBMA [10].

Jiang and his coworker proposed a revised criterion which is a function of three variables (1) the intrinsic viscosity of the polymeric components (2) the weight fractions (3) the difference of the cross Huggins coefficient for the polyblend and geometric average of Huggins coefficient for the constituent polymers. The revised criterion gave good results by using six binary blend systems [11].

Yan Pan and his coworkers put a new viscometric criterion for polymer-polymer interaction and it was found that this is quite reasonable when it is compared with the results of the previous studies. He proposed a K term, an apparent association constant which is a function of intrinsic viscosity and weight fraction of the components [12].

Imren and her coworkers used the viscometric method to search the compatibilization effect of maleic anhydride-styrene-vinyl acetate terpolymer on PVC/EVA blends in the range of 0.5-2.0 g/dl in THF solvent. The interaction parameter delta b is used to study the miscibility and compatibility of polymer blend in solution, obtained from the modified Krigbaum and Wall theory [13].

In the present work, as distinct from literature, short oil alkyd and iBMA/MMA copolymer blend compatibility is investigated by viscosimetry.

3. THEORY

3.1 Free Radical Polymerization

Polymers are produced from monomer reactions where monomer must have the functionality greater than or equal to 2. This functionality can be derived from; opening of a double bond, opening of a ring, or coreactive functional groups [14].

The world production of polymers by free radical polymerization is in the range 100 million tons per year. This is nearly %50 of all synthetic polymers. Because of this production capacity, free radical polymerization is one of the most studied chemical processes [15].

Like all chain reactions, it involves three fundamental steps: initiation, propagation, and termination. In addition, a fourth step called chain transfer may be involved [14].

Initiator decomposition	$I_2 \xrightarrow{k_d} 2I^{\bullet}$
Chain Initiation	$I^{\bullet} + M \xrightarrow{k_i} R_1^{\bullet}$
Chain Propagation	$R_i^{\bullet} + M \xrightarrow{k_p} R_{i+1}^{\bullet}$
Chain Transfer	$R_i + S \xrightarrow{k_{tr}} R_1^{\bullet} + P_i$
Chain Termination	$R_i + R_j \xrightarrow{k_{t,c,d}} P_{i+j} \ or \ P_i + P_j$

(Where $R_i^\bullet$ is a radical of chain length i, I_2 is the initiator, M is the monomer, S is a transfer agent, and P is polymer).

3.1.1 Initiation

Gain of an active site by the monomer represents initiation. The absorption of heat, light (ultraviolet), or high-energy irradiation causes initiation. Initiation of free radical polymerization is often brought about by the addition of small quantities of compounds called initiators. Reaction is an unimolecular decomposition and k_d will be a first order rate constant. The magnitude of this decomposition rate constant is usually of the order of $10^{-4} – 10^{-6}$ sec^{-1} at the temperatures at which such initiators are used [14].

The rate of initiation $R_i \bullet$ is the rate of reaction. This can be expressed in terms of the rate of radical production as;

$$R_i = 2 f k_d [I] \qquad (2.1)$$

where f , the fraction of all radicals generated that are captured by monomers, is called the *initiator efficiency*[14].

3.1.2 Propagation

Propagation steps are reactions which products are formed, and the site of the reactive centre changes. The number of active centres is not changed. Atom transfer and addition reactions are two major propagation reactions [6].

Addition Reactions can be represented as;

$$M_1^{\bullet} + M \longrightarrow M_2^{\bullet}$$

$$M_2^{\bullet} + M \longrightarrow M_3^{\bullet}$$

$$M_i^{\bullet} + M \longrightarrow M_{i+1}^{\bullet}$$

The rate of propagation R_p is given by;

$$R_p = k_p[M^{\bullet}][M] \qquad (2.2)$$

where [M] stands for the sum of the concentrations of all monomer- ended radicals in the system.

Atom transfer reactions in free-radical polymerizations are called *chain transfer reactions* [14].

3.1.3 Termination

The direct coupling is a mode of termination that gives a dead polymer with combination of two free radicals. The rate coefficient is $k_{t,c}$.

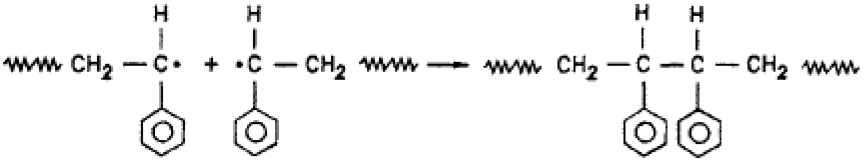


Figure 3.1: Example of termination by combination [14].

When a hydrogen atom is transferred from one of the radical chain ends to another radical, two stabilized polymer chains carrying a double bond are obtained. This reaction is associated with the rate coefficient $k_{t,d}$ [15].

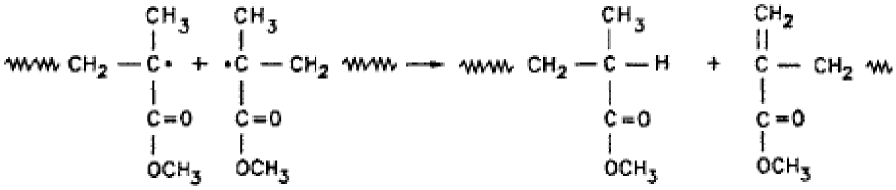


Figure 3.2: Example of termination by disproportionation [11].

The overall rate constant k_t given by;

$$k_t = k_{tc} + k_{td} \qquad (2.3)$$

From rate equations of disproportionation and combination;

$$R_t = 2k_t[M^\bullet]^2 \qquad (2.4)$$

Typical termination rate constants are of the order of 10^6-10^8 litre/mol sec. These rate constants are much greater than k_p, but polymerization still occurs because the overall rate of polymerization is proportional to k_p and inversely proportional to $k_t^{1/2}$ [14].

3.1.4 Rate of Polymerization

The approximations that are made in its derivation are *(i)* chain length and conversion independent rate coefficients k_t and k_p;

(ii) instantaneous establishment of a steady-state free radical concentration;

(iii) monomer is only consumed by chain propagation and not via the initiation process or chain transfer. This assumption allows to equate the rate of the loss of monomer with the rate of polymerization;

(iv) all reactions are irreversible;

(v) the effective concentration of initiator-derived free radicals is constant throughout the polymerization.

The kinetic chain length v; is the average number of monomers that react with an active centre from its formation until it is terminated. It is given by the ratio of the rate of polymerization to the rate of initiation and under steady-state conditions where $R_\mathrm{t} = R_i$ [15].

$$v = \frac{R_p}{R_i} = \frac{k_p[M][M^\bullet]}{2fk_d[I]} = \frac{k_p[M][M^\bullet]}{2k_t[M^\bullet]^2} \tag{2.5}$$

from equations 2.1, 2.2 and 2.4. Therefore,

$$v = \frac{k_p[M]}{2k_t[M^\bullet]} = \frac{{k_p}^2[M]^2}{2k_tR_p} \tag{2.6}$$

by substituting for $[M^{\bullet}]$ from equation 2.2.

If the polymerization is initiated by thermal homolysis of an initiator,

$$v = \frac{k_p[M]}{2(fk_d[I]k_t)^{1/2}} \tag{2.7}$$

The number average degree of polymerization, $\overline{DP}_n$, is equal at any instant to the ratio of the rate of monomer disappearance to the rate at which completed polymer molecules are produced. That is,

$$\overline{DP}_n = -\frac{d[M]}{dt} \Big/ \frac{d[polymer]}{dt} \tag{2.8}$$

$$\frac{d[polymer]}{dt} = k_{tc}[M^{\bullet}]^2 + 2k_{td}[M^{\bullet}]^2 \tag{2.9}$$

because each termination reaction by combination yields one polymer molecular while each disproportionation produces two macromolecules. Equations 2.2 and 2.9 can be substituted into Equation 2.8 to yield

$$\overline{DP}_n = \frac{k_p[M]}{(k_{tc} + 2k_{td})[M^{\bullet}]} \tag{2.10}$$

and with $[M^{\bullet}] = R_p \big/ k_p[M]$ from equation 2.2,

$$\overline{DP}_n = \frac{{k_p}^2[M]^2}{R_p(k_{tc} + 2k_{td})} \tag{2.11}$$

Also, for initiation by thermal homolysis of an initiator,

$$\overline{DP}_n = \frac{k_p[M](k_{tc}+k_{td})^{1/2}}{(k_{tc}+2k_{td})(fk_d[I])^{1/2}} = \frac{k_p[M](k_{tc}+k_{td})^{1/2}}{(k_{tc}+2k_{td})\left(\frac{1}{2}R_i\right)^{1/2}} \qquad (2.12)$$

3.1.5 Chain Transfer

Because of chain stopping events via chain transfer reactions, the measured average molecular weights of polymers generated by free radical polymerization processes are often lower than those predicted by accounting for initiation, propagation, and termination processes [15].

The ideal free-radical kinetics without chain transfer culminates in Equations 2.11 and 2.12 which termination of the growth of polymeric radicals is accounted or only by mutual reaction of two such radicals. Chain transfer can also end the physical growth of macro radicals, and the polymerization model will now be mended to include the latter process. This can be easily done by changing Equation 2.8 to include transfer reactions in the rate of polymer production, *d[polymer]/dt.* Combining Equations 2.8 and chain transfer reaction,

$$d[polymer]/dt = k_{tc}[M^\bullet]^2 + 2k_{td}[M^\bullet]^2 + k_{tr}[M^\bullet][TH] \qquad (2.13)$$

If we substitute Equation 2.13 into 2.8 and invert the resulting expression (for ease in manipulation), it is written as;

$$\frac{1}{\overline{DP}_n} = \frac{k_{tc}[M^\bullet]}{k_p[M]} + \frac{2k_{td}[M^\bullet]}{k_p[M]} + \frac{k_{tr}[TH]}{k_p[M]} \qquad (2.14)$$

Then putting $[M^{\bullet}] = R_p / k_p[M]$ from Equation 2.2;

$$\frac{1}{\overline{DP}_n} = \frac{k_{tc} R_p}{k_p{}^2 [M]^2} + \frac{2k_{td} R_p}{k_p{}^2 [M]^2} + \frac{k_{tr}[TH]}{k_p[M]} \tag{2.15}$$

It is customary to define *a chain transfer constant C* for transfer agent as the ratio of k_{tr} for that material with a propagating radical to k_p for that radical. Thus,

$$C \equiv \frac{k_{tr}}{k_p} \tag{2.16}$$

In this notation, Equation 2.15 is written

$$\frac{1}{\overline{DP}_n} = \frac{k_{tc} R_p}{k_p{}^2 [M]^2} + \frac{2k_{td} R_p}{k_p{}^2 [M]^2} + C\frac{[Ta]}{[M]} \tag{2.17}$$

3.1.6 Suspension Polymerization

Suspension polymerization referred to as bead or pearl polymerization. The monomer (discontinuous phase) as droplets (50-500 mm in diameter) is suspended in the water as continuous phase. The water: monomer weight ratio varies from 1:1 to 4:1 in most polymerizations. Coalescing of the monomer droplets (subsequently converted to polymer particles) is prevented by agitation and the presence of suspension stabilizers [16].

In suspension polymerizations the initiators must be soluble in the monomer droplets. They are referred to as oil-soluble initiators. Each monomer droplet in a suspension polymerization is considered to be a miniature bulk polymerization system. The kinetics of polymerization within each droplet are the same as those for the corresponding bulk polymerization [16].

3.2 Copolymerization

Polymers contain more than one type of monomer in the polymer chain are called as copolymers Figure 2.3. shows the polymers that fall into this category.

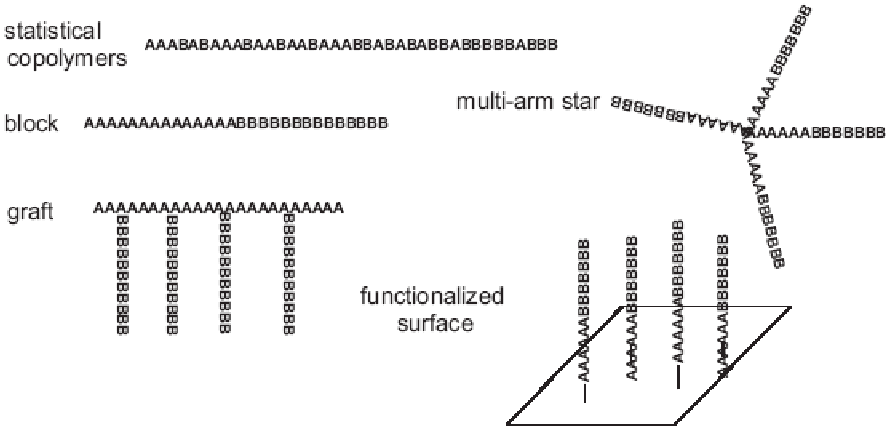


Figure 3.3: Types of copolymers [17].

3.2.1 Copolymerization Equation and Reactivity Ratios

Possible propagation reactions at any stage in the copolymerization can be shown as;

$$i)\quad \sim M_1^{\bullet} + M_1 \xrightarrow{k1,1} \sim M_1 - M_1^{\bullet}$$

$$ii)\quad \sim M_1^{\bullet} + M_2 \xrightarrow{k1,2} \sim M_1 - M_2^{\bullet}$$

$$iii)\quad \sim M_2^{\bullet} + M_1 \xrightarrow{k2,1} \sim M_2 - M_1^{\bullet}$$

$$iv)\quad \sim M_2^{\bullet} + M_2 \xrightarrow{k2,2} \sim M_2 - M_2^{\bullet}$$

The rate of formation of radicals by initiation is equal to termination of radicals by termination in the steady state.

$$R_i = R_t$$

$$k_{21}[\sim M_2^{\bullet}][M_1] = k_{12}[\sim M_1^{\bullet}][M_2] \qquad (2.18)$$

The rate of consumption of M_1 is;

$$-\frac{d[M_1]}{dt} = k_{1,1}[\sim M_1^{\bullet}][M_1] + k_{2,1}[\sim M_2^{\bullet}][M_1] \qquad (2.19)$$

The rate of consumption of M_2 is;

$$-\frac{d[M_2]}{dt} = k_{1,2}[\sim M_1^\bullet][M_2] + k_{2,2}[\sim M_2^\bullet][M_2] \tag{2.20}$$

From equation 2.18;

$$[\sim M_1^\bullet] = \frac{k_{2,1}[\sim M_2^\bullet][M_1]}{k_{1,2}[M_2]} \tag{2.21}$$

Substituting for $[\sim M_1^\bullet]$ in equations 2.19 and 2.20;

$$-\frac{d[M_1]}{dt} = \frac{k_{1,1}k_{2,1}[\sim M_2^\bullet][M_1]^2}{k_{1,2}[M_2]} + k_{2,1}[\sim M_2^\bullet][M_1] \tag{2.22}$$

and

$$-\frac{d[M_2]}{dt} = \frac{k_{1,1}k_{2,1}[\sim M_2^\bullet][M_1][M_2] + k_{2,2}[\sim M_2^\bullet][M_2]}{k_{1,2}[M_2]} \tag{2.23}$$

$$-\frac{d[M_2]}{dt} = [\sim M_2^\bullet](k_{2,1}[M_1] + k_{2,2}[M_2]) \tag{2.24}$$

then

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](\frac{k_{1,1}}{k_{1,2}}[M_1] + [M_2]}{[M_2](\frac{k_{2,2}}{k_{2,1}}[M_1] + [M_2]} \tag{2.25}$$

Replacing $\frac{k_{1,1}}{k_{1,2}}$ with r_1 and $\frac{k_{2,2}}{k_{2,1}}$ with r_2,

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1\frac{[M_1]}{[M_2]}+1)}{[M_2](\frac{[M_1]}{[M_2]}+r_2)} \tag{2.26}$$

r_1 is the reactivity of M_1 with respect to M_1 and M_2 and r_2 is the reactivity of M_2 with respect to M_2 and M_1. The equation is known as the copolymer composition equation. By calculation, this equation is used to predict the composition of a polymer resulting from the polymerization of M_1 and M_2.

It is possible to calculate feed ratios of monomers to obtain a given copolymer composition provided r_1 and r_2 are known.

Using the equation;

$$F_1 = \frac{\left(r_1 f_1^{\,2} + f_1 f_2\right)}{\left(r_1 f_1^{\,2} + 2 f_1 f_2 + r_2 f_2^{\,2}\right)} \tag{2.27}$$

Where F_1 is the mole fraction of monomer M_1 in the increment of polymer formed at a given stage in the copolymerization and f_1 is the mole fraction of unreacted monomer M_1 in the feed and

$$f_1 = \left(1 - f_2\right) \tag{2.28}$$

Table 3.1: Copolymer Structure and r_1r_2 Product [14].

r_1	r_2	r_1r_2	Copolymer Structure
$r_1=1/r_2$	$r_2=1/r_1$	1	Random(ideal)
<<1	<<1	$\rightarrow 0$	Alternating
>>1	<1	<1	Tends to be homopolymer of M_1

3.3 Chain-growth Copolymerization

Using chain-growth polymerization for copolymerization of two or more monomers is an effective way of changing the balance of properties of commercial polymers [14].

Unsaturated monomers are converted to polymers through chain reactions. In chain polymerization processes, the active centre is retained at the end of a growing polymer chain and monomers are added to this centre in rapid succession. The rate of addition of monomers to the active centre relative to the overall conversion of the monomer to polymer is quite fast. This means that high-molecular-weight polymers are generated even while most of the monomers remain unreacted [18].

3.4 Compatibility

When any two materials are mixed together, or blended, the properties of the resulting mixture depend on the level at which intimate mixing takes place and on whether any chemical reactions between the components of the mixture take place.

If there is no phase separation, we can talk about existence of a miscible polymer blend. In a miscible polymer blend, there must be miscibility and homogeneity that extend down to the molecular level. If an immiscible blend is a useful blend wherein the inhomogeneity caused by the different phases is on a small enough scale not to be apparent in use, it can be called compatible. Polymer blends that are miscible in certain useful ranges of composition and temperature, but immiscible in others, are also sometimes called compatible blends [19].

3.4.1 Solubility Parameters

The Gibbs free energy of mixture of two substances A and B must be less than the sum of the Gibbs free energies of separate constituents. This means that ΔG_{mix}, the increase in free energy on mixing should be $\Delta G_{mix} < 0$. The free energy is given by G = H - TS, where H is the enthalpy and S is the entropy, so that the necessary condition for mixing at temperature T is;

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} < 0 \quad (2.29)$$

where ΔH_{mix} is the enthalpy of mixing and ΔS_{mix} is the entropy of mixing. Attraction between molecules A and A and molecules B and B is usually stronger than attraction between molecules A and B. Rarely there are special attractive forces, such as hydrogen-bonding, between molecules of the two different types A and B. If A and B molecules mix randomly, $\Delta H_{mix} > 0$. For this hypothetical random mixing, ΔH_{mix} per mole is usually written in the form;

$$\Delta H_{mix} = RT\chi_{AB} v_A v_B \quad (2.30)$$

where v_A and v_B are the volume fractions of molecules A and B. χ_{AB} is the Flory–Huggins interaction parameter[19].

When an ideal solution is obtained from its components, volume change will be zero ($\Delta V_{mix} = 0$) or enthalpy change ($\Delta H_{mix} = 0$) will be zero. So, the properties of ideal solutions depend entirely on entropy effects and

$$\Delta G_{mix} = -T\Delta S_{mix} \tag{2.31}$$

If ΔH_{mix} is not required to be zero, a so-called "regular solution" is obtained. All deviations from ideality are ascribed to enthalpic effects. Nonzero ΔH_{mix} values are assumed to be caused by the net results of breaking solvent (1-1) contacts and polymer (2-2) contacts and making polymer-solvent (1-2) contacts [20].

The total contact energy of the system E is the sum of the energies for (1-1) and (2-2) contacts plus half the sum of the expressions for (1-2) contacts (because we have counted the latter once in connection with N_1species 1 molecules and again with reference to the N_2 species 2 molecules):

$$E = \frac{c_1\omega_{11}N_1{}^2v_1 + \omega_{12}N_1N_2(c_1v_2 + c_2v_1) + c_2\omega_{22}N_2{}^2v_2}{2(N_1V_1 + N_2V_2)} \tag{2.32}$$

Where N_i is total of molecules of species, v_i is molecular volume, c_i is contacts of molecule with other molecules. Each contact contributes interaction energy ω_{ii}.

Equation 2.32 can be manipulated to

$$E = N_1\left(\frac{1}{2}c_1\omega_{11}\right) + N_2\left(\frac{1}{2}c_2\omega_{22}\right) + \frac{1}{2}\frac{N_1N_2}{N_1v_1 + N_2v_2} \times[\omega_{12}(c_1v_2 + c_2v_1) - \omega_{11}c_1v_2 - \omega_{22}c_2v_1] \tag{2.33}$$

To eliminate ω_{12} it is assumed that ω_{12} to be equal to the geometric mean of ω_{11} and ω_{22}.

$$\frac{1}{2}\omega_{12}\left(\frac{c_1}{v_1} + \frac{c_2}{v_2}\right) = \left[\frac{c_1\omega_{11}}{v_1}\frac{c_2\omega_{22}}{v_2}\right]^{1/2} \tag{2.34}$$

Then

$$E = N_1\frac{c_1\omega_{11}}{2} + N_2\frac{c_2\omega_{22}}{2} - \frac{N_1N_2v_1v_2}{N_1v_1 + N_2v_2}\left[\left(\frac{c_1\omega_{11}}{2v_1}\right)^{1/2} - \left(\frac{c_2\omega_{22}}{2v_2}\right)^{1/2}\right]^2 \tag{2.35}$$

If the contact energies can be assumed to be independent of temperature, the enthalpy change on mixing, ΔH_{mix}, is then

$$\Delta H_{mix} = \Delta U_{mix} = \frac{N_1N_2v_1v_2}{N_1v_1 + N_2v_2}\left[\left(\frac{c_1\omega_{11}}{2v_1}\right)^{1/2} - \left(\frac{c_2\omega_{22}}{2v_2}\right)^{1/2}\right]^2 \tag{2.36}$$

The terms in $(c_i\omega_{ii}/2v_i)^{1/2}$ are solubility parameters and are given the symbol δ_i. Equation 2.41 is then;

$$\begin{aligned}\Delta H_{mix} &= [N_1 N_2 v_1 v_2 /(N_1 v_1 + N_2 v_2)][\delta_1 - \delta_2]^2 \\ &= (N_1 v_1 / V)(N_2 v_2 / V)[\delta_1 - \delta_2]^2 V = V\phi_1\phi_2[\delta_1 - \delta_2]^2\end{aligned} \qquad (2.37)$$

where the ϕ_i are volume fractions. Hence the heat of mixing per unit volume of mixture is

$$\Delta H_{mix} / V = \phi_1\phi_2[\delta_1 - \delta_2]^2 \qquad (2.38)$$

Since ΔS_{mix} is always positive, the components of a mixture are assumed to be compatible only if $\Delta H_{mix} \leq T\Delta S_{mix}$. So if there exists zero or small value of ΔH_{mix}, solution will be compatible. We must remember that that this theory allows only endothermic mixing. In general, then, miscibility is predicted if the absolute value of the $(\delta_1 - \delta_2)$ difference is zero or small [20].

3.4.2 Flory-Huggins Model for Polymer-Polymer Mixtures

The mixing together of two or more polymers is an established method used to arrive at new property combinations without having to synthesize new structures with the desired characteristics.

The Flory–Huggins (FH) model introduces the concept of a reference segment volume V_R. It is the smallest polymer repeat unit.. FH model is developed for polymer solutions but can be extended to polymer/polymer mixtures. For a binary polymer mixture, the combinatorial entropy of mixing ΔS_{mix} can be expressed as; [20]

$$\frac{\Delta S_{mix}}{R} = -\left(\frac{V}{V_R}\right)\left[\frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2\right] \qquad (2.39)$$

where r_i is the number of segments per chain molecule (the degree of polymerization) of component i relative to V_R, ϕ_i is the corresponding volume fraction, and V is the total molar volume of the two components[20].

For a binary mixture of two polymers, the Gibbs free energy of mixing can be obtained from Equation 2.39,

$$\frac{\Delta G_m}{RT} = \left(\frac{V}{V_R}\right)\left[\frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2 + \phi_1\phi_2\chi_{12}\right] \tag{2.40}$$

The critical value of the interaction parameter can be estimated from Equation 2.40, by differentiation:

$$\chi_{12} = 0.5\left[\frac{1}{\sqrt{r_1}} + \frac{1}{\sqrt{r_2}}\right]^2 \tag{2.41}$$

The critical value above which the two polymers phase separate can be determined from Equation 2.41 for mixtures of low molecular weight with $r_1 = r_2$. χ_{12} can be compared to the corresponding difference in solubility parameters, as shown in Table 3.2. The tolerated difference between the solubility parameters for miscibility to be achieved decreases with r_1 and r_2, for high molecular weight polymers to mix, the solubility parameter must be very close. For example, polystyrene ([δ = 18.4 (J/cm3)0.5] and poly(α-methyl styrene) [δ = 18.1 (J/cm3)0.5] are predicted to be miscible up to M_n ~60000 while for miscibility to be achieved between poly(methyl methacrylate) [δ = 19.0 (J/cm3)0.5] and poly(methyl acrylate) [δ = 19.6 (J/cm3)0.5] M_n needs to be lower than

13000. Miscibility is expected to be strongly molecular/weight–dependent [20].

Table 3.2: Critical Values of the Interaction Parameters χ_{12c} as a Function of Molecular Weight and Comparison to the Required Difference between the Polymer Solubility Parameters, $(\delta_1 - \delta_2)_{critical}$ [20].

$m_1=m_2$	χ_{12}	$(\delta_1-\delta_2)_{critical}$ $(J/cm^2)^{1/2}$
50	0.04	1.00
500	0.004	0.31
5000	0.0004	0.10

3.4.3 Compatibility Investigation

The polymer-polymer compatibility investigations are made by many experimental and theoretical methods and some of the most important techniques for polymer-polymer compatibility are thermal analysis, electron microscopy, dynamic mechanical studies and viscometric techniques. An effective, quick and inexpensive method for investigation of polymer-polymer interactions is the viscometric measurement. Therefore this technique is used for many polymer pairs to determine their miscibility [6].

The viscous flow of a polymer solution involves a shearing action in which different layers of the solution move with differing velocities. There is a pronounced increase in the viscosity of a polymer solution relative to that of the pure solvent even at low concentrations of the polymer. In this respect, the polymer solute behaves as a colloidal dispersion, which is known to retard the flow of adjacent layers of a liquid under shearing force. For spherical colloidal particles, the viscosity of the solution, η, relative to that of the pure solvent, η_0, is referred to as the relative viscosity, given by

$$\eta_r = \eta / \eta_0 \tag{2.42}$$

The viscosity of a liquid or solution can be measured by using a viscometer whose design is based on the Hagen–Poiseuille law. Essentially, this involves the measurement of the flow rate of the liquid through a capillary tube which is part of the viscometer. Consequently, by measuring the flow time of the solution, t, and that of the pure solvent, t_0, the relative viscosity can be determined:

$$\eta_r = \eta / \eta_0 = t / t_0 \tag{2.43}$$

As indicated above, the viscosity of the polymer solution is always greater than that of the pure solvent. This fractional increase in the viscosity resulting from the dissolved polymer in the solvent is referred to as the specific viscosity η_{sp}, given by

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1 \tag{2.44}$$

The specific viscosity normalized with respect to the concentration, η_{sp}/C, is referred to as the reduced specific viscosity or, simply, reduced viscosity. It measures that capacity with which a given polymer enhances the specific viscosity. The intrinsic viscosity $[\eta]$ is the limiting value of the reduced viscosity at infinite dilution: [21]

$$[\eta] = \lim_{c \longrightarrow 0} \eta_{sp} / c \qquad (2.45)$$

Polymers possess the unique capacity to increase the viscosity of the solvent in which they are dissolved. Within a homologous series of linear polymers, the higher the molecular weight the greater the increase in viscosity for a given polymer concentration. In other words, this capacity to enhance viscosity or intrinsic viscosity is a reflection of the molecular weight of the dissolved polymer.

The linear relation between log[η] and log M may then be written as;

$$[\eta] = KM^{a} \qquad (2.46)$$

Where K and a are constants determined from the intercept and slope of plots of intrinsic viscosity versus molecular weight. The relation given in Equation (2.46) is referred to as the Mark–Houwink equation.

It must be reemphasized that the Mark–Houwink equation applies to fractionated samples of a given polymer. This means that, strictly speaking, it covers only a narrow molecular weight range. However, it is relatively easier in practice to use intrinsic viscosity measurements for the determination of the molecular weights even for unfractionated polymers. For such molecularly heterogeneous polymers, the appropriate relation becomes;

$$[\eta] = K\overline{M}_{v}^{a} \qquad (2.47)$$

Where $\overline{M}_v$ is the viscosity average molecular weight.

The concentration of viscosity of the dilute solution is given by the classical Huggins equation;

$$\eta_{sp} = [\eta]c + bc^2 \tag{2.48}$$

Where $[\eta]$ is intrinsic viscosity, c is a concentration and b is related to the Huggins coefficient, k reflects binary interactions between polymer segments.

$$b = k[\eta]_{mix}^2 \tag{2.49}$$

Equation (2.49) extended by Krigbaum and Wall can be applied to polymer mixtures in a common solvent. The total concentration ($c = c_1 + c_2$) is introduced as,

$$\eta_{spm} = [\eta]_m (c_1 + c_2) + b_m (c_1 + c_2)^2 \tag{2.50}$$

Subscripts 1, 2 and m represent polymer 1, polymer 2, and polymer blends, respectively. b_m is related to the Huggins parameter, k_m of the polymer blend as,

$$b_m = k_m [\eta]_m^2 \tag{2.51}$$

$[\eta]_m$ is the weight average of intrinsic viscosity of the two-component polymer mixture. The experimental values of $[\eta]_m^{\exp}$ can be determined by extrapolation to infinite dilution of the plots and the values of $b_m^{\exp}$ can be obtained from the slopes of the plots according to Equation (2.50). The criterion $\Delta[\eta]_m$ based on the difference between the experimental and ideal values of $[\eta]_m$ have proposed by Garcia et al. as follows

$$\Delta[\eta]_m = [\eta]_m^{\exp} - [\eta]_m^{id} \tag{2.52}$$

$\Delta[\eta]_m < 0$ and $\Delta[\eta]_m > 0$ values show miscibility and immiscibility, respectively. $[\eta]_m^{id}$ is the intrinsic viscosity of the ideal solution introduced as follows:

$$[\eta]_m^{id} = w_1[\eta]_1 + w_2[\eta]_2 \tag{2.53}$$

where, w_1 and w_2 are the weight fractions of polymer 1 and 2, respectively. $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities of the pure polymer solutions.

4. EXPERIMENTAL STUDY

4.1. Materials

4.1.1. Monomers

MMA: Monomers are received from Akzo Nobel Kemipol. $C_5H_8O_2$; MW : 100 g/mol, Density : 0,94 g/cm^3, Boiling point : 101°C.

n-BMA: Monomer is received from Akzo Nobel Kemipol. $C_8H_{14}O_2$; MW : 142 g/mol, Density : 0,9 g/cm^3, Boiling point : 163°C

i-BMA: Monomer is received from Akzo Nobel Kemipol. $C_8H_{14}O_2$; MW : 142 g/mol, Density : 0,88 g/cm^3, Boiling Point : 155°C

4.1.2. Initiators

BPO: Benzoyl Peroxide, $C_{14}H_{10}O_4$, MW : 242 g/mol

AIBN: Azobisisobutyronitrile, $C_8H_{12}N_4$, MW : 164 g/mol

4.1.3. Others

Short (less than 40%) oil Alkyd: Alkyd is received from Akzo Nobel Kemipol.

PVA as dispersant: $(C_2H_4O)_x$

Benzyl Mercaptan as chain transfer agent: $C_6H_5CH_2SH$, origin is Merck Company, MW : 124 g/mol, Boiling point : 194°C, Density : 1,05 g/cm^3.

4.2. Methods

4.2.1. Polymerizations

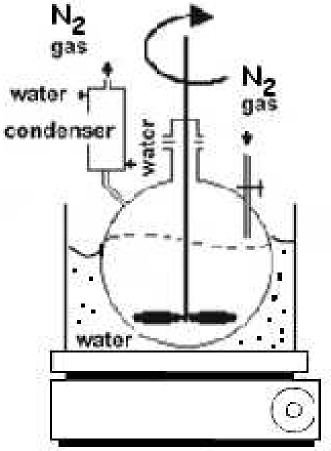


Figure 4.1: Schematic representation of the reactor (250 ml) used for suspension polymerization.

Suspension polymerizations were carried out in a 250 ml three-necked round bottom flask with a mechanical stirrer under nitrogen atmosphere(1.30 lt/min). Reaction temperature was stabilized at 85±2°C with hot water bath. A water condenser was equipped for recovery of monomers which have boiling points 101°C and 155°C.

Monomers, water (continuous phase) and dispersant were fed into the system at the same time. Initiator and the chain transfer agent were fed before heating up the system. Reaction times were kept above 60 minutes for gaining minimum %80 conversions. Summary of polymerizations are shown in Table 4.1.

Table 4.1: Summary of polymerization reactions.

RUN	Monomers [g.]				Initiators [g.]		Transfer Agent [g.]
	Mole Frac. %MMA	MMA	n-BMA	i-BMA	BPO	AIBN	Benzyl Mercaptan
1	68	15	10	-	0,25	-	-
2	68	15	-	10	0,25	-	-
3	68	15	-	10	-	0,25	-
4	68	15	-	10	-	0,5	-
5	68	7,5	-	5	-	0,125	0,3
6	68	7,5	-	5	-	0,125	0,15
7	68	7,5	-	5	-	0,125	0,05
8	60	6	-	5,7	-	0,125	-
9	50	5	-	7,1	-	0,125	-

4.2.2. Analysis of Copolymers

4.2.2.1. Viscometric Analysis

Copolymer samples were dried in an oven at 40°C for 24h before Leo Ubbelohde Viscometer measurements were taken. Copolymers were diluted with toluene at different concentration.

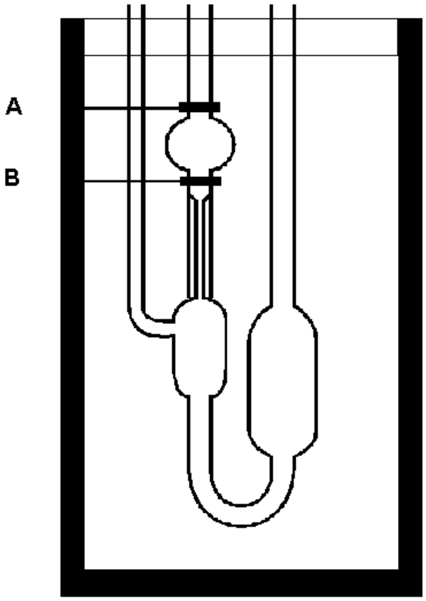


Figure 4.2: Schematic representation of Ubbelohde viscometer used for measurements.

4.2.2.2. DSC and Infrared Spectrometer Analysis

DSC analyses were done by TA Instrument 2910 MDSC V4.4E at Polinas R&D Laboratory. Copolymer Run#4 (68/32 molar ratio of monomer feed), Copolymer Run#8 (60/40 molar ratio of monomer feed), Copolymer Run#9 (50/50 molar ratio of monomer feed), and commercial sample were heated from 25°C to 100°C at a speed 2°C/minute.

Infrared Spectrophotometer spectra were taken with Shimadzu Model IR-470. Spectra were acquired at 8 cm^{-1} resolution in the spectral range 400 – 4000 cm^{-1}.

5. RESULTS AND DISCUSSION

5.1. Intrinsic Viscosity of Alkyd and Copolymer Samples

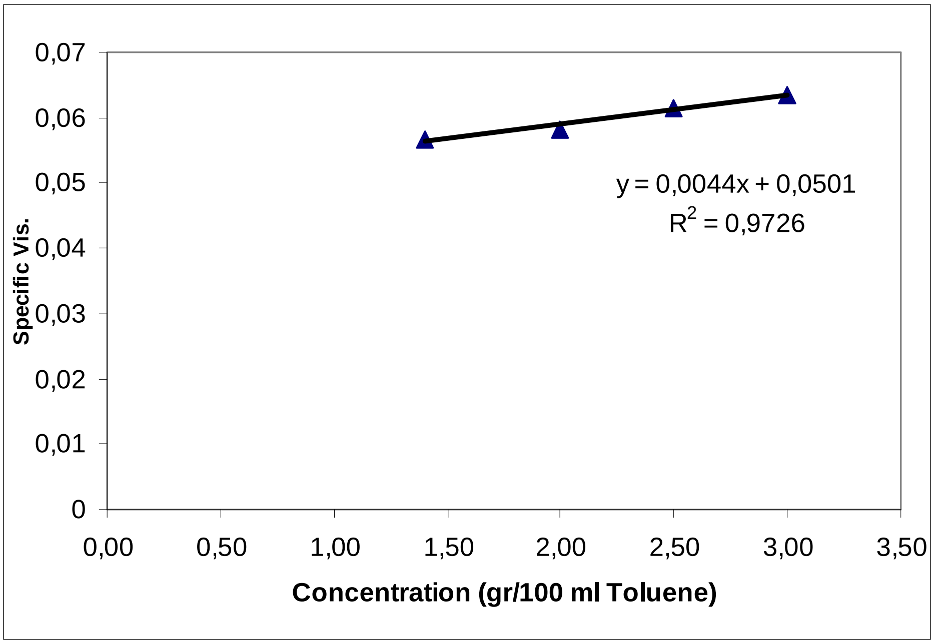


Figure 5.1: Specific viscosity of Short oil Alkyd (η_{int} = 0,050 dl/g).

Intrinsic viscosity measurement of short oil alkyd solutions with respect to concentration is shown in Figure 5.1. All products of polymerizations were measured by Ubbelohde viscometer and [η] values were calculated. Viscosity measurement details of copolymer Run#5 where $T_{Toluene}$ is 189 seconds, is given in Table 5.1 Results of intrinsic viscosity measurements are shown in Table 5.2.

Table 5.1: Viscosity measurement details of copolymer Run#4.

Concentration (gr/100 ml)	Time Measured (Seconds)	Relative Viscosity	Specific Viscosity
1,5	487	2,577	1,051
1,25	430	2,275	1,02
1,0	372	1,968	0,968
0,75	317	1,677	0,903
0,5	271	1,434	0,868

Table 5.2: Results of intrinsic viscosity measurements.

Name	Intrinsic Viscosity [dl/g]	R^2
Copolymer Run#1	0,959	0,997
Copolymer Run#2	1,408	0,987
Copolymer Run#3	1,040	0,956
Copolymer Run#4	0,762	0,977
Copolymer Run#5	0,001	0,989
Copolymer Run#6	0,034	0,964
Copolymer Run#7	0,099	0,940
Copolymer Run#8	0,864	0,998
Copolymer Run#9	0,720	0,999
Commercial Sample	0,398	0,962

5.2. Molecular Weight Effect on Compatibility

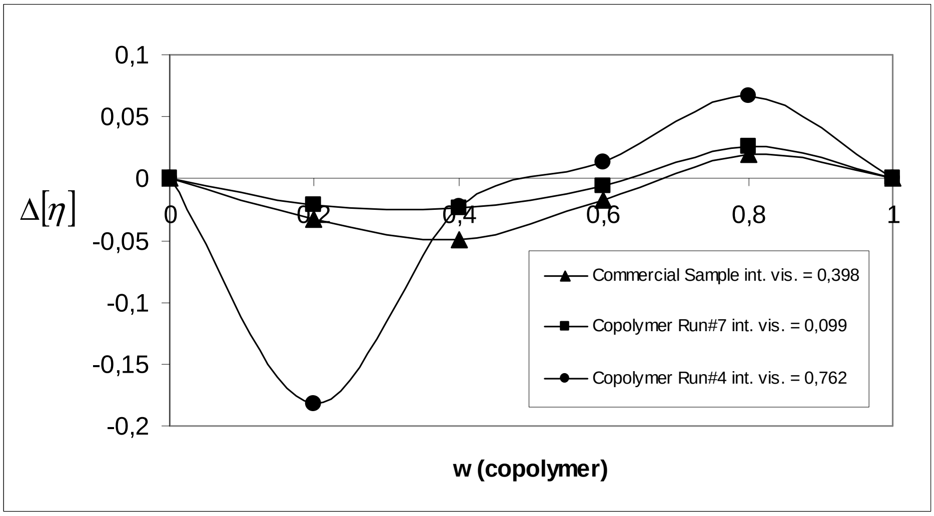


Figure 5.2: Compatibility test by viscosity measurement (Molecular weight effect).

Weight fraction of polymers in polymer-alkyd blend versus $\Delta[\eta]_m = [\eta]_m^{\exp} - [\eta]_m^{id}$ is shown in Figure 5.2. Commercial sample, Copolymer Run#7 and Copolymer Run#4 has different intrinsic viscosity values as 0,398, 0,099, and 0,762. The higher the molecular weight the greater the increase in viscosity for a given polymer concentration. In other words, this capacity to enhance viscosity or intrinsic viscosity is a reflection of the molecular weight of the dissolved polymer. It is assumed that K and a value of Mark–Houwink Equation for copolymer runs differ at a narrow range because of structural similarities, so intrinsic viscosity measurements provide a tool for characterization of polymer molecular weight. From the intrinsic viscosity values of these copolymer, we can put in order by molecular weight $MW_{Copolymer\#5} > MW_{CommercialSample} > MW_{Copolymer\#8}$.

Figure has shown that lower molecular weight copolymer run#8 has better compatibility with short oil alkyd. It is compatible at several compositions (20/80, 40/60, and 60/40). Copolymer run#4 which has higher molecular weight than copolymer run#7, is only compatible at 20/80 and 40/60. The commercial sample is also compatible at 20/80, 40/60, and 60/40.

A particular polymer mixture can be made more miscible by reducing the molecular weights of the components. From Equation (2.39) any measure that increases the entropy of mixing ΔS_{mix} will favour a more negative ΔG_{mix} The Flory-Huggins theory shows that the entropy gain on mixing a polymer is inversely related to its number average size.

5.3. Feed Ratios Effect on Compatibility

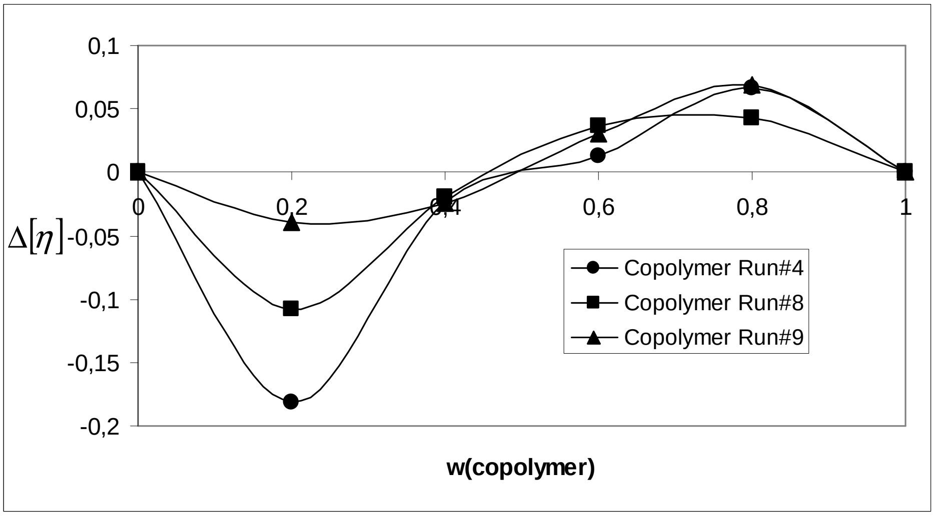


Figure 5.3: Compatibility test by viscosity measurement (Feed ratio effect).

Weight fraction of polymers in polymer-alkyd blend versus $\Delta[\eta]_m = [\eta]_m^{\exp} - [\eta]_m^{id}$ is shown in Figure 5.3. Copolymer Run#4, Copolymer Run#8 and Copolymer Run#9 has different monomer molar feed ratios as 68/32, 60/40, and 50/50. Intrinsic viscosities of copolymers are 0,762, 0,864, and 0,720. All runs are compatible at 20/80 and 40/60 with short oil alkyd. It can be seen from Figure 5.3 that there is no change at compatibility compositions when molar feed ratio of MMA was decreased from 0,68 to 0,5.

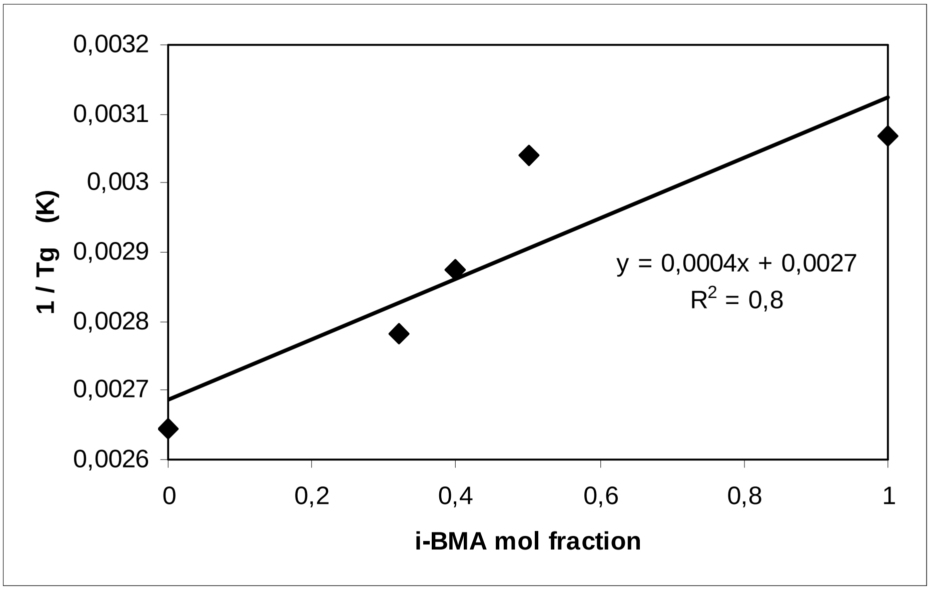


Figure 5.4: Tg values of copolymers vs molar ratio of i-BMA in the copolymer [22].

The Figure 5.4 shows that T_g of the copolymer decreases with the increase of molar ratio of i-BMA in the polymer chains. Low T_g values for a binder is important because of the improvement in flexibility of the paint film. But increasing molar feed ratio of i-BMA in suspension polymerizations will scale up molar ratio of i-BMA in the copolymer composition because reactivity ratio of i-BMA is threefold of reactivity ratio of MMA. Reactivity ratios of monomers are $r_{MMA} = 0{,}62$ $r_{iBMA} = 1{,}88$. [22]

A convenient form of copolymer composition equation (2.27) is;

$$F_1 = \frac{1 + r_1\chi}{2 + r_1\chi + r_2/\chi} \qquad (5.1)$$

Where $\chi = f_1 / f_2$.

F_{MMA}, mole fraction of MMA in copolymer is calculated using equation 5.1 and reactivity ratios r_1=0,62 and r_2=1,88. Calculated values from Equation 5.1 are plotted as Figure 5.5.

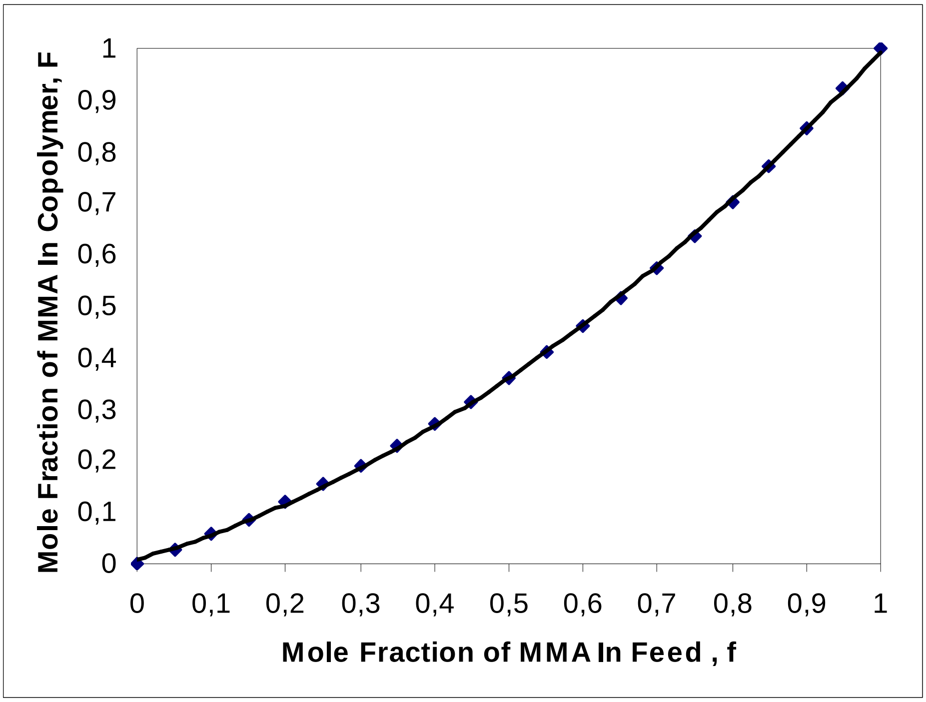


Figure 5.5: Relation between instantaneous feed composition f_{MMA} and corresponding copolymer composition F_{MMA} for MMA and i-BMA copolymerization.

As shown in Figure 5.5, copolymer structure tends to be random (ideal) when $r_1 r_2 \cong 1$.

5.4. Chain Transfer Effect on Molecular Weight

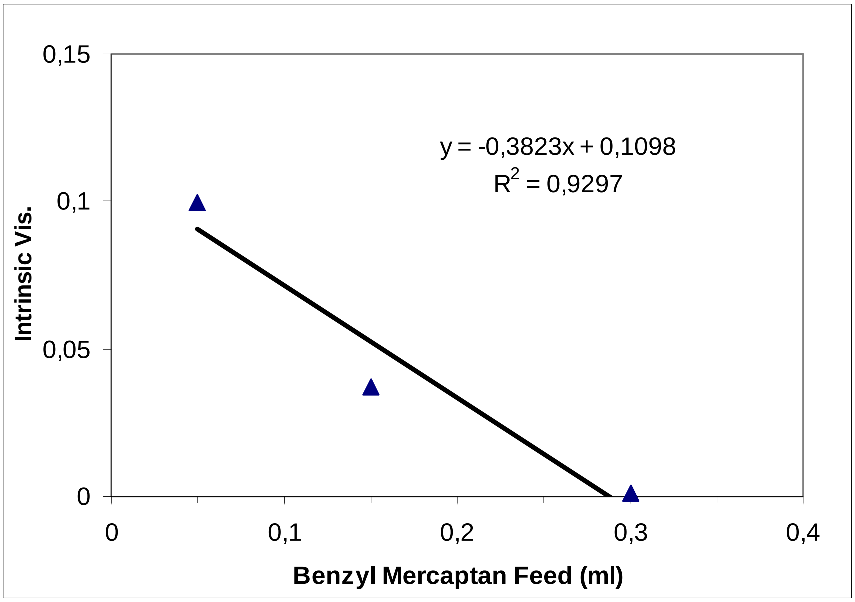


Figure 5.6: Chain transfer agent feed (ml) effect on intrinsic viscosity.

Benzyl mercaptan as transfer agent feed into reactor versus intrinsic viscosity of copolymer is shown in Figure 5.6. Increase of intrinsic viscosity of copolymer can be seen with the decrease of chain transfer feed. As mentioned before, intrinsic viscosity measurements provide a tool for characterization of polymer molecular weight. However, it is hard to determine intrinsic viscosity values under 0,1 because of practical time measurement difficulties.

6. CONCLUSIONS

In this study the compatibility behavior of poly(methylmethacrylate-co-isobutylmethacrylate) with alkyd resin blend was examined by using dilute solution viscometry method.

Copolymers were prepared in the laboratory by changing the feed ratios of monomers and the concentration of chain transfer agent. Suspension polymerization was the method of polymerization preferred since it was a method which could easily be used in large scale polymerizations as well. Nine runs of suspension polymerizations were carried out for investigation of the effects of molecular weight and feed ratio on compatibility.

Copolymers 4, 8, and 9 were prepared with three different feed ratios of MMA and i-BMA as 68/32, 60/40, and 50/50 respectively. It is revealed that difference in monomer composition in the polymer chain did not change the compatibility of the copolymer with the alkyd resin. The compatibility range of these two polymeric materials changes between 0 and 60% of the copolymer weight fraction in the mixture. General application range is known to be 50/50 of the acrylic and alkyd resin, so laboratory prepared acrylic polymer seems to give satisfactory results. It is a well known fact that acrylic polymers have excellent weathering properties, so they are preferred in outdoor applications. In the literature the agreement of the viscometric results and the thermal analysis support the validity of viscometric studies [12]. Further studies might be focused on this subject as well as investigation of film properties of the laboratory prepared copolymers.

Chain transfer agent Benzyl mercaptan was used to lower the molecular weight of the copolymers. It is shown that molecular weight of the copolymer is inversely related to its entropy gain on mixing as the Flory-Huggins theory points out. Increasing the entropy gain gives negative Gibbs free energy to obtain compatible alkyd copolymer blends.

Yearly production capacity of industrial coatings is 200.000 tonnes in Turkey. 5% of this capacity would be alkyd-acrylic copolymer blend. Acrylics which are imported from USA and Europe are used to obtain improvement of drying-time, film clarity, and film flexibility [22].

7. REFERENCES

1. **Wicks, Zeno W., Frank N. Jones** (2007). *Organic Coatings, 3rd Ed.*. Canada.: John Wiley & Sons, Inc. Publication
2. **Tracton, A**. (July 28, 2005). *Coatings Technology Handbook, Third Edition* . Bridgewater, New Jersey, USA : Marcel Dekker.
3. **Forsgren, Amy** (Apr. 2006). *Corrosion Control Through Organic Coatings* . Florida,USA: CRC Press .
4. **Bentley, J.** (1987). *Paint and Surface Coatings*. Chichester,England: Ellis Horwood.
5. **Garcia, R., Melad O., Gomez C.M.** (1999).Viscometric study on the compatibility of polymer-polymer mixtures in solution. *European Polymer Journal, 35,* 47-55.
6. **Aroguz A.Z., Baysal, B.M.** (2006).Miscibility studies on blends of poly(phenyleneoxide)/brominated polystyrene by viscometry. *European Polymer Journal*, *42*, 311-315.
7. **Wanchoo R.K. and Sharma P.K.** (2003). Viscometric study on the compatibility of some water soluble polymer-polymer mixture. *European Polymer Journal*, *39,* 1481-1490.
8. **Pingping Z.** (1997). A new criterion of polymer-polymer miscibility detected by viscometry. *European Polymer Journal*, *33,* 411-413.
9. **Aroguz A.Z., Kismir Y.** (2007).Viscometric study on the miscibility of polystyrene/brominated polystyrene blends. *European Polymer Journal, 43*, 410-415.
10. **Chee K. K.** (1990). Determination of polymer-polymer miscibility by viscometry, *European Polymer Journal*, *26,* 423-426.
11. **Jiang W.H. and Han S.** (1998). An improved criterion of polymer-polmer miscibility determined by viscometry. *European Polymer Journal*, 1579-1584.
12. **Pan Y., Cheng R., Xue F., and Fu W.** (2002). A new viscometric criterion for polymer-polymer interaction, *European Polymer Journal*, *38,* 1703-1708.
13. **Imren D.,Boztug A.,Yilmaz E.,Zengin B.** (2008). Viscometric investigation of compatibilization of the poly(vinyl chloride)/poly(ethylene-co-vinyl acetate) blends by terpolymer of

maleic anhydride-styrene-vinyl acetate, *Journal of Molecular Structure, 891(1-3),* 329-332.

14. **Rudin, Alfred** (September 1998). *Elements of Polymer Science and Engineering*. Elsevier Science & Technology Books.
15. **Encyclopedia of Polymer Science and Technology, Radical Polymerization**, 3rd Ed., Ed. J.I.Kroschwitz, John Wiley & Sons, Inc., New York, (2005)
16. **Odian, George** (2004). *Principles of Polymerization. 4th edition*. Staten Island, New York: John Wiley & Sons, Inc. Publication
17. **Davis, Kelly A.** (March 2002). *Statistical, Gradient, Block, and Graft Copolymers by Controlled Living Radical Polymerizations*. New York: Springer.
18. **Ebewele, Robert O.** (March 23, 2000). *Polymer Science and Technology,* Chapter 7. ,Benin City, Nigeria
19. **Bower, David I.** (2002). *An Introduction to Polymer Physics*. United Kingdom: Cambridge University Press.
20. **Encyclopedia of Polymer Science and Technology, Miscibility**, Ed. J.I.Kroschwitz, John Wiley & Sons, Inc., New York, (2005)
21. **Ebewele, Robert O.** (March 23, 2000). *Polymer Science and Technology,* Chapter 12. ,Benin City, Nigeria.
22. **Brandrup, J.** (1998). *Polymer Handbook*. John Wiley & Sons.
23. **Private Communication**, Gizli A., Akzo Nobel Kemipol A.S., Izmir , Turkey.

APPENDICES

APPENDIX A : Viscosity Measurements Data.

APPENDIX B : DSC Graphs of Copolymers.

APPENDIX C : FTIR Spectra of Copolymers.

APPENDIX A

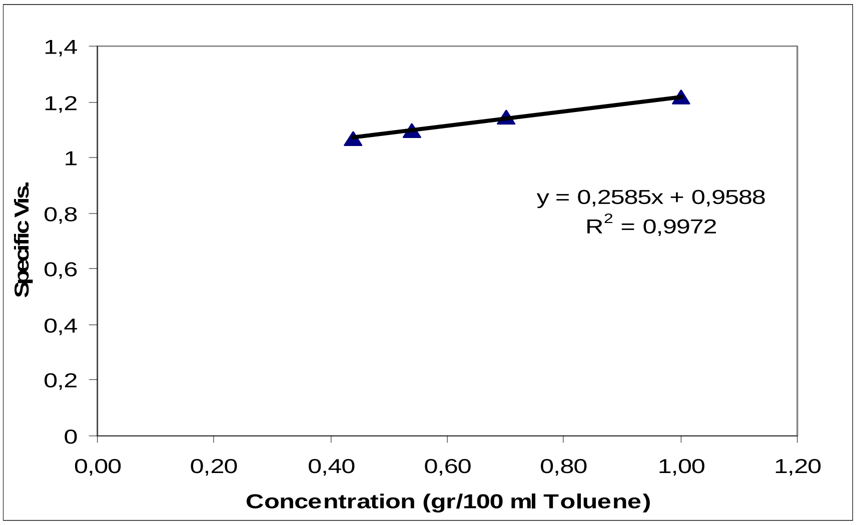


Figure A.1: Specific viscosity of Copolymer Run#1 (η_{int} = 0,959 dl/g).

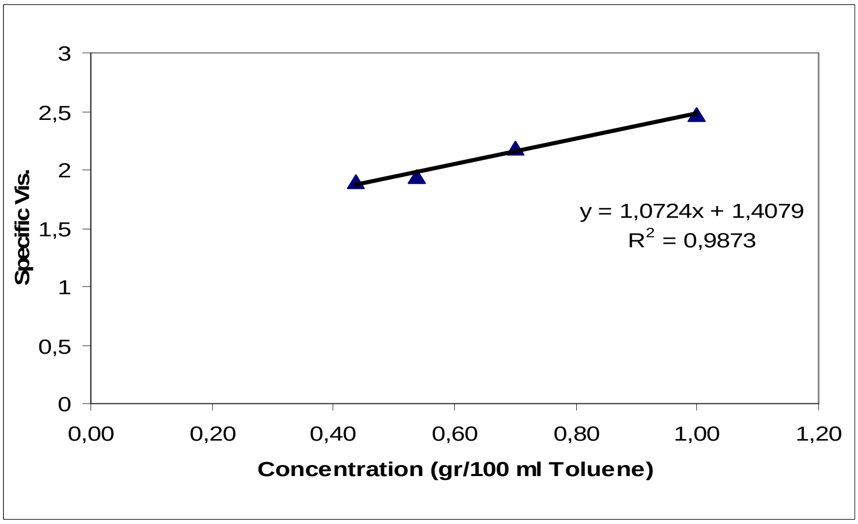


Figure A.2: Specific viscosity of Copolymer Run#2 (η_{int} = 1,408 dl/g).

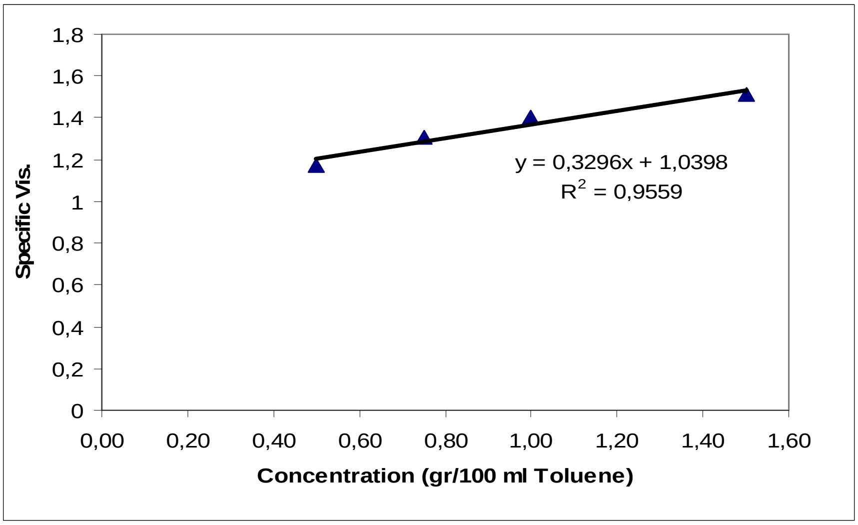


Figure A.3: Specific viscosity of Copolymer Run#3 (η_{int} = 1,040 dl/g).

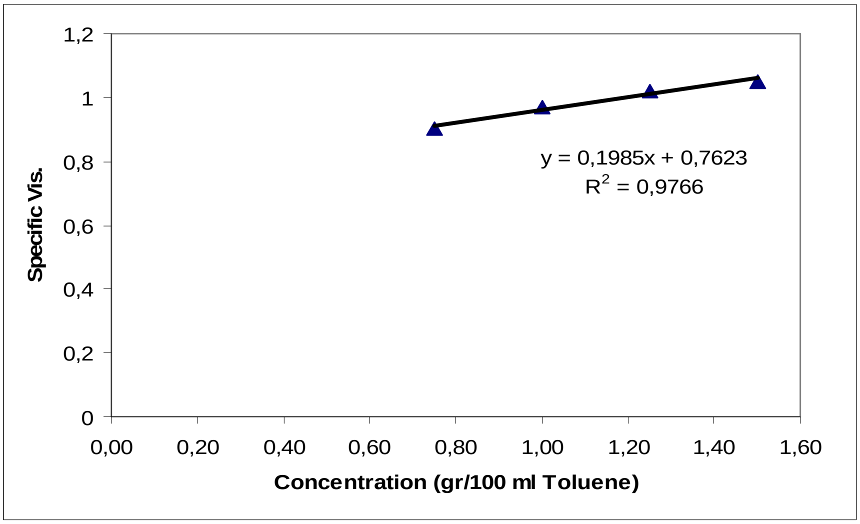


Figure A.4: Specific viscosity of Copolymer Run#4 (η_{int} = 0,762 dl/g).

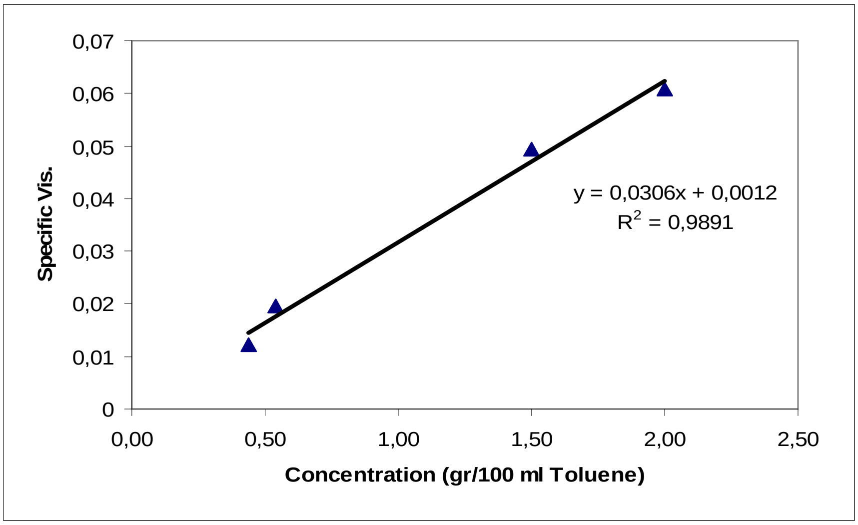


Figure A.5 Specific viscosity of Copolymer Run#5 (η_{int} = 0,001 dl/g).

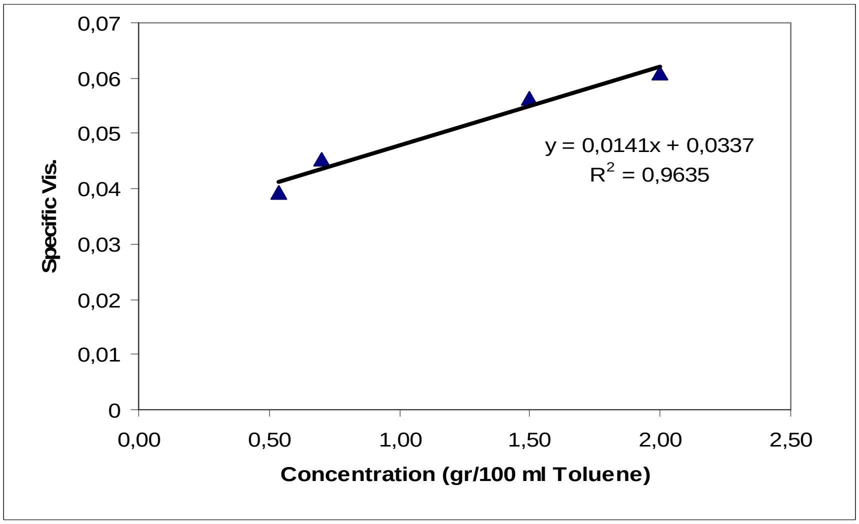


Figure A.6: Specific viscosity of Copolymer Run#6 (η_{int} = 0,034 dl/g).

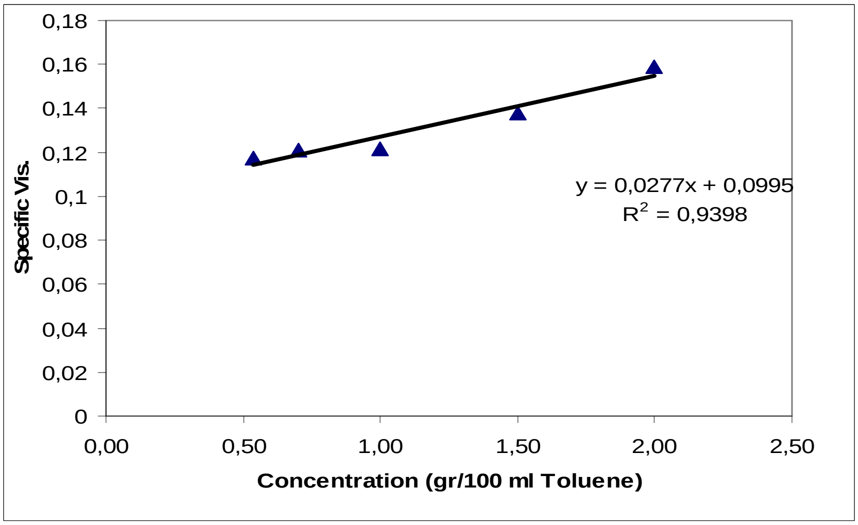


Figure A.7: Specific viscosity of Copolymer Run#7 (η_{int} = 0,099 dl/g).

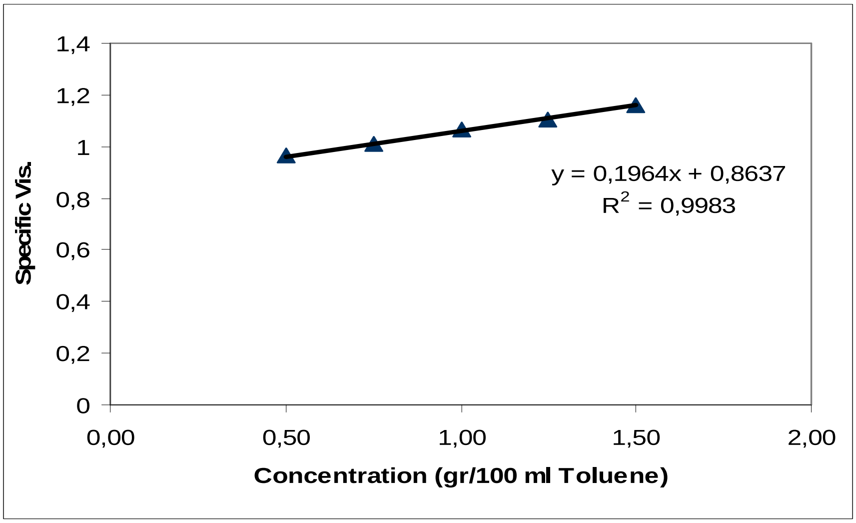


Figure A.8: Specific viscosity of Copolymer Run#8 (η_{int} = 0,864 dl/g).

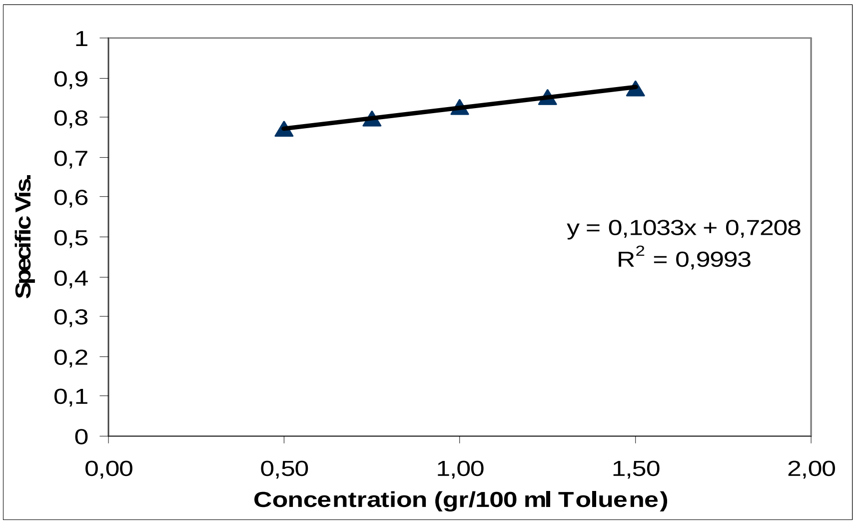


Figure A.9: Specific viscosity of Copolymer Run#9 (η_{int} = 0,721 dl/g).

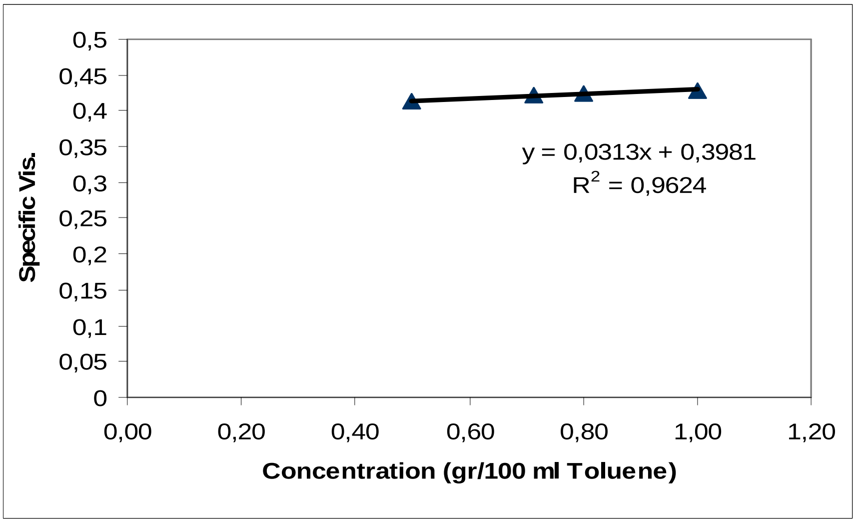


Figure A.10: Specific viscosity of Commercial Sample (η_{int} = 0,398 dl/g).

Table A.1: Viscosity measurement data of copolymers.

RUN	Concentration [gr/100 ml Toulene]	$T_{solution}$ [s]	Specific Viscosity	RUN	Concentration [gr/100 ml Toulene]	$T_{solution}$ [s]	Specific Viscosity
1	1,00	412	1,215	7	2,00	249	0,159
1	0,70	335	1,144	7	1,50	228	0,138
1	0,54	296	1,098	7	1,00	212	0,122
1	0,44	273	1,069	7	0,70	205	0,121
2	1,00	646	2,473	7	0,54	201	0,118
2	0,70	471	2,189	8	1,50	518	1,160
2	0,54	381	1,947	8	1,25	450	1,105
2	0,44	340	1,892	8	1,00	390	1,063
3	1,00	435	1,513	8	0,75	332	1,009
3	0,70	342	1,402	8	0,50	280	0,963
3	0,54	300	1,305	9	1,50	437	0,875
3	0,44	271	1,175	9	1,25	390	0,851
4	1,50	487	1,051	9	1,00	345	0,825
4	1,25	430	1,020	9	0,75	302	0,797
4	1,00	372	0,968	9	0,50	262	0,772
4	0,75	317	0,903	CS	1,00	270	0,429
5	2,00	212	0,061	CS	0,80	253	0,423
5	1,50	203	0,049	CS	0,71	246	0,422
5	0,54	191	0,020	CS	0,50	228	0,413
5	0,44	190	0,012	-	-	-	-
6	2,00	212	0,061	-	-	-	-
6	1,50	205	0,056	-	-	-	-
6	0,70	195	0,045	-	-	-	-
6	0,54	193	0,039	-	-	-	-

CS : Commercial Sample

Table A.2: Viscosity measurement data of compatibility tests a) Copolymer Run#7 vs. Alkyd b) Copolymer Run#4 vs. Alkyd c) Copolymer Run#8 vs. Alkyd d) Copolymer Run#9 vs. Alkyd.

	Alkyd %	Concentration [gr/100 ml Toulene]	$T_{solution}$ [s]	Specific Viscosity		Alkyd %	Concentration [gr/100 ml Toulene]	$T_{solution}$ [s]	Specific Viscosity
a	20	5,00	320	0,139	**b**	20	1,25	398	0,885
	20	4,17	296	0,136		20	1,00	348	0,841
	20	3,33	272	0,132		20	0,74	300	0,799
	20	2,63	253	0,129		20	0,50	262	0,772
	40	5,00	297	0,114		40	2,00	425	0,624
	40	4,17	275	0,109		40	1,56	365	0,596
	40	3,33	253	0,102		40	1,25	325	0,576
	40	2,63	237	0,097		40	1,00	295	0,561
	60	5,00	276	0,092		60	3,57	539	0,519
	60	4,17	259	0,089		60	2,94	458	0,484
	60	3,33	242	0,084		60	2,38	392	0,451
	60	2,63	224	0,070		60	1,92	344	0,426
	80	5,00	252	0,067		80	5,00	414	0,238
	80	4,17	242	0,067		80	4,17	368	0,227
	80	3,33	227	0,060		80	3,33	323	0,213
	80	2,63	217	0,056		80	2,63	292	0,207
c	20	1,25	406	0,919	**d**	20	1,25	356	0,707
	20	1,00	359	0,899		20	1,00	320	0,693
	20	0,74	307	0,849		20	0,74	284	0,684
	20	0,50	266	0,815		20	0,50	253	0,677
	40	2,00	430	0,638		40	2,00	400	0,558
	40	1,67	387	0,629		40	1,67	361	0,546
	40	1,33	345	0,619		40	1,33	324	0,536
	40	1,05	310	0,608		40	1,05	293	0,523
	60	3,57	525	0,498		60	3,57	484	0,437
	60	2,94	457	0,482		60	2,94	419	0,414
	60	2,38	393	0,453		60	2,38	365	0,391
	60	1,92	351	0,446		60	1,92	324	0,371
	80	5,00	312	0,130		80	5,00	387	0,210
	80	4,17	290	0,128		80	4,17	347	0,201
	80	3,33	267	0,124		80	3,33	309	0,190
	80	2,63	249	0,121		80	2,63	279	0,181

Table A.3: Viscosity measurement data of compatibility test of commercial Sample.

Alkyd %	Concentration [gr/100 ml Toulene]	$T_{solution}$ [s]	Specific Viscosity
20	2,50	377	0,398
20	2,08	344	0,394
20	1,67	310	0,384
20	1,32	282	0,374
40	3,57	447	0,382
40	3,13	400	0,357
40	2,63	358	0,340
40	2,08	317	0,325
60	5,00	495	0,324
60	4,17	420	0,293
60	3,33	354	0,262
60	2,63	308	0,239
80	5,00	325	0,144
80	4,17	298	0,138
80	3,33	270	0,129
80	2,63	248	0,119

APPENDIX B

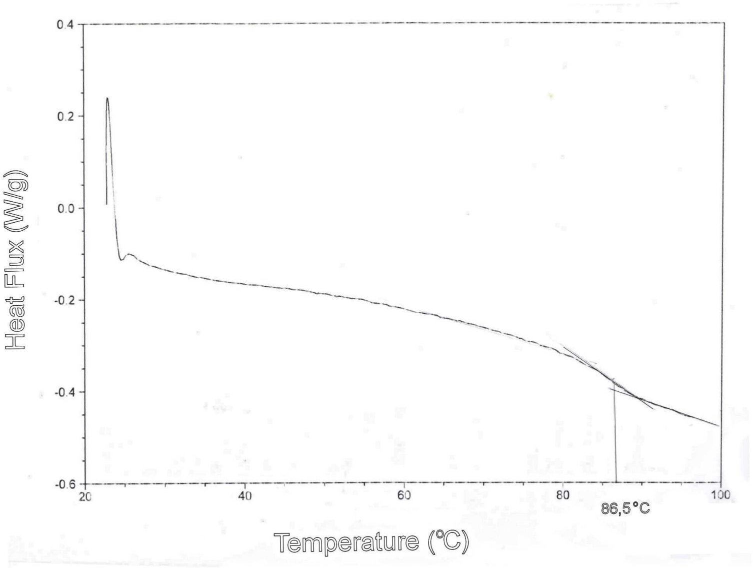


Figure B.1: DSC analysis of Copolymer Run#4 (T_g = 86,5 °C).

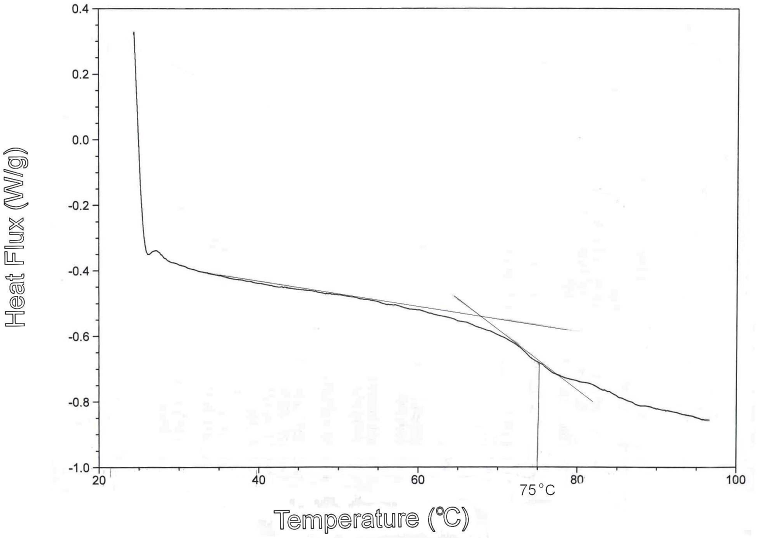


Figure B.2: DSC analysis of Copolymer Run#8 (T_g = 75 °C).

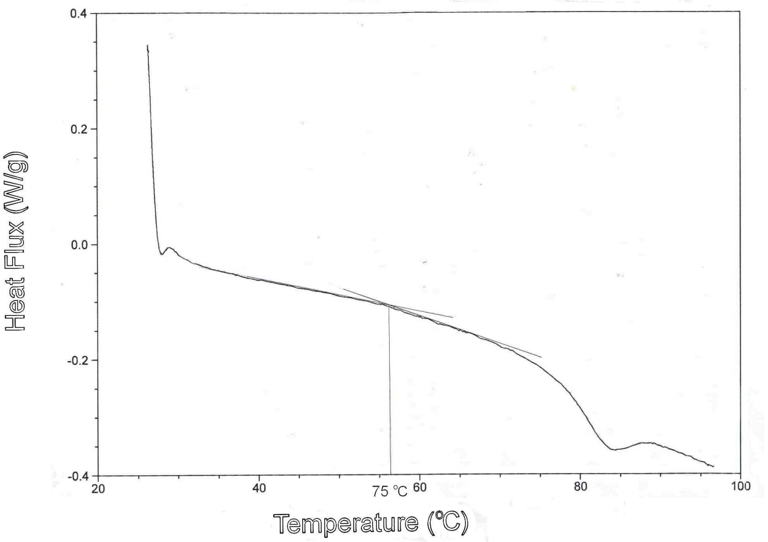


Figure B.3: DSC analysis of Copolymer Run#9 (T_g = 56 °C).

APPENDIX C

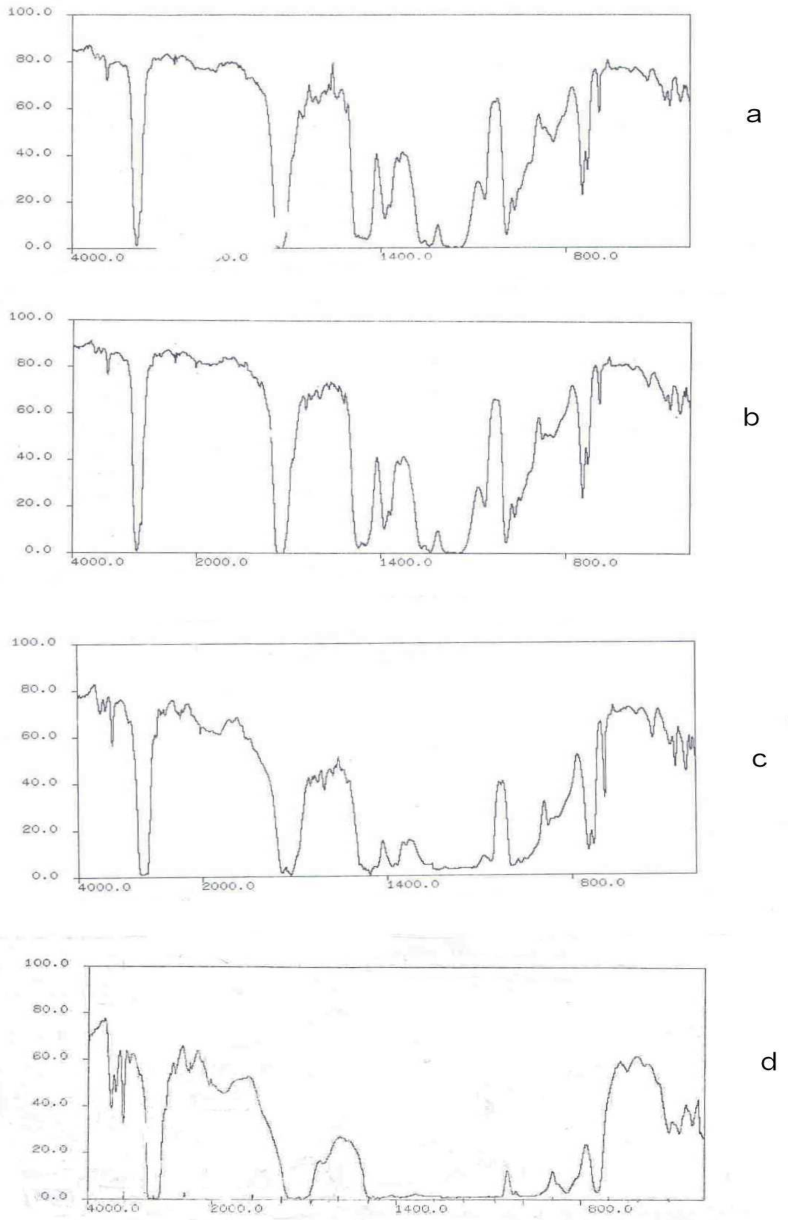


Figure C.1: FTIR Spectra of Copolymers a) Copolymer Run#4 b) Copolymer Run#8 c) Copolymer Run#9 d) Commercial Sample.