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Pour Point Depressant and Thermal Properties of Copolymers of Lauryl Methacrylate and Styrene Synthesized via Atom Transfer Radical Polymerization

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ABSTRACT

Random copolymers of lauryl methacrylate and styrene using EBiB /CuBr/ OPMI(initiator/ catalyst/ ligand) initiation system. The thermal stability of the copolymer increased with increasing amount of styrene in copolymers but it decreases the solubility of the copolymers in the base oil and copolymers with higher styrene content shows low PPDs properties. The reactivity ratios obtained from EVM method $r_S = 0.53$, $r_{LMA} = 0.65$.

Keywords--- Random copolymer, ATRP, Reactivity Ratio, Pour Point Depressant.

I.   INTRODUCTION

Copolymers based on alkyl methacrylates are widely used as additives in modifying the rheology of lubricanting oils, where they serve as viscosity thickeners, viscosity index improvers and pour point depressants. Most frequently, they are long-chained, linear polymers consisting of monomers with a changeable share of lateral alkyl groups, mostly C_1-C_{18}. It was established that the methacrylates with medium-size lateral alkyl groups enhances the viscosity index and the pour point of solutions while the methyl group contributes to the stiffness of polymer chain. The corresponding monomer unit ratio is optimized to assure the best properties for a given application. Besides composition, the properties of an additive also depend on copolymer structural parameters such as molar mass and molar mass distribution. Such polymers, apart from exhibiting high solution viscosities and viscosity index values, should also be stable against the high shear stress that arises in lubricating conditions over a broad temperature range and heavy mechanical loads. Recently, the development of methacrylic additives has been directed towards multifunctional activity and improvement of its thermal and oxidative stability as well as resistance against mechanical breakdown. These were achieved by building, in small amounts, of a functional or stabilizing comonomer into polymeric chains during the course of synthesis. Commonly used comonomers of such type are maleic anhydride, maleic acid esters, maleimides, N-vinyl pyrrolidone, N-vinyl imidazole, styrene and its derivatives.[1-4] From the earlier studies on styrene–based methacrylate additives (mostly copolymers of butyl or decyl methacrylate), particularly those conducted by Akhmedov et al.[5] shows that these additives possess higher thermal stability and improved shear stability in comparison to poly(alkyl methacrylates). These improvements are facilitated by increasing the styrene content but application of copolymers containing high styrene content is limited by their relatively low solubility in mineral oils.

The pour point is the lowest temperature below which the base oil cannot flow. The majority of crude oils contain a large amount of oil waxes called paraffin. The base oil also has substantial amounts of paraffin because it is produced in the refining process of crude oil. Paraffins are mixtures of hydrocarbons with linear chains that contain mainly 20–40 carbon atoms in addition to alkanes with branched and cyclic chains.[6] The solubility of paraffins present in the base oil decreases with decreasing temperature. Consequently, the first crystal appears at a certain temperature, called the cloud point or wax appearance temperature.[7-9] As the temperature decreases below this point, paraffin crystals grow and form platelets, needles and orthorhombic structures. They overlap and interlock with each other and thereby form three-dimensional networks. The oil remaining around this network gets trapped in it and form a gel like structure.[9-12]This gel becomes sufficiently dense with further cooling, which cause oil to solidify apparently. Upon further decrease in temperature, the complexity of the structure increases and finally the movement of oil ceases at the pour point.[13] Paraffin deposition is one of the most important problems with base oil, which consists mostly of paraffinic oil when it is applied under low-temperature conditions. The intensive dewaxing of oil during refining can reduce the pour point of the base oil. However, this

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procedure decreases the oxidation stability of the oil and increases its tendency to deposit carbon. Addition of PPDs to the base oil is a reasonable solution to this problem. There are some characteristics of additives that must be considered when they are being used to reduce the pour point: (i) there must be a sufficient number of pendant alkyl groups with sufficiently long hydrocarbon chains; (ii) there must be an appropriate distance between the hydrocarbon pendant chains and (iii) there must be a suitable ratio of monomers when a copolymer is used.

In this paper we polymerize the mixture of LMA/ styrene by ATRP method using CuBr/ OPMI/ EBiB (catalyst/ ligand/ initiator) initiation system. Choudhary.et.al[14] carried out the homogeneous polymerization of LMA using CuBr/ OPMI/ EBiB system. The copolymers thus prepared were characterized using GPC (molecular weight and molecular weight distribution), NMR (structural characterization), TGA (thermal stability) and DSC (glass transition temperature). The monomer reactivity ratios were determined by both Kelen-Tudos (KT)[15] and nonlinear error-in-variables (EVM)[16-17] methods. These copolymers were also evaluated as pour point depressants.

II. EXPERIMENTAL DETAILS

2.1 Materials

Lauryl methacrylate, LMA (Aldrich, USA, 96%) was purified by washing with 5% aqueous NaOH solution, followed by washing with water till neutral and then dried over anhydrous $CaCl_2$. Finally it was distilled under vacuum and stored in refrigerator below 5^oC. Styrene (G. S. Chemicals, Bombay, 99.5%) was purified by stirring over CaH_2 under nitrogen then distilled from it at reduced pressure before use.

Copper bromide, (Aldrich USA, 98%) was purified by stirring in glacial acetic acid under nitrogen followed by filtration, washing with dry ethanol and dried at 100^oC.

Ethyl-2-bromo-isobutyrate (EBiB) (Aldrich USA, 98%), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) (Aldrich USA, 99%) were used as received.

Toluene (Merck) was dried and purified by refluxing with sodium and benzophenone under nitrogen followed by distillation.

The base oil, which had a Saybolt universal second of 150 was supplied by the Indian Oil Corporation Limited (IOCL), Faridabad, India

2.2 Synthesis of Poly(styrene-co-LMA) Copolymer

For this purpose, styrene and LMA were polymerized using [EBiB]: [CuBr]: [OPMI] as initiator: catalyst: ligand 100: 1: 1: 2.5. For ATRP polymerization, a dry schlenk tube was filled with CuBr (0.0585g, 0.408 mmol), OPMI (0.2227g, 1.02 mmol) and monomer mixture [100: 1: 1: 2.5] in that order. The reaction mixture was purged with nitrogen for 15 minutes to remove traces of oxygen. The tube was degassed three times by repeated freeze/ vacuum/ thaw cycles and finally evacuated and back filled with nitrogen. The reaction mixture was placed in preheated oil bath at 95^oC. The initiator ethyl-2-bromoisobutyrate (0.0585mL, 0.408mmol) was added to the reaction mixture in the schlenk tube. The polymerization was stopped at a desired time by cooling the tube in ice water. The reaction mixture was diluted with toluene and passed through a short neutral alumina column to remove the catalyst. The polymer was precipitated with methanol and separated by filtration. The polymer was then dried under vacuum for 24h at 60^oC and yield was determined gravimetrically. Several copolymer samples were prepared by varying the molar ratio of monomers (styrene: LMA) in the initial feed. The detailed feed composition along with sample designation is given in Table 1.1.

For kinetic studies, polymer samples were taken out at different intervals of time to observe the change in molecular weight with conversion. The reaction was quenched by precipitation in methanol.

Table.1.1: Details of feed composition in the preparation of copolymers.

Sample Designation	Mole fraction of styrene in feed (f_1)	Mole fraction of LMA in feed (f_2)	Mole fraction of monomers in copolymer	
			(F_1)	(F_2)
PS/PLMA 80/20	0.80	0.20	0.74	0.26
PS/PLMA 60/40	0.60	0.40	0.54	0.46
PS/PLMA 50/50	0.50	0.50	0.46	0.54
PS/PLMA 40/60	0.40	0.60	0.39	0.61
PS/PLMA 20/80	0.20	0.80	0.22	0.78

F_1=styrene and F_2=LMA in copolymers

III. CHARACTERIZATION

3.1 Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR spectra were recorded on a Bruker spectrospin DPX 300 spectro-meter (Fallenden, Switzerland) using $CDCl_3$ as a solvent and tetramethylsilane (TMS) as an internal standard.

3.2 Gel Permeation Chromatography (GPC)

Waters (1525) gel permeation chromatograph (Milford, MA) equipped with styragel (HR-3 and HR-4, 7.8x 300 mm) columns along with Evaporating Light Scattering Detector (ELSD-2420) was used to determine the molecular weight and molecular weight distribution in polymers. For calibration, polystyrene standards (Shodex Standards SL-105, Japan) having molecular weight of 197,000, 51,000, 13,900 and 2100 were used. THF was used as solvent at a flow rate of 1 mL/min.

3.3 Thermal Characterization:

Thermal characterization was done using thermogravimetry and differential scanning calorimetry. TA 2100 thermal analyzer was used for recording TG/DTG traces in nitrogen atmosphere over the temperature range of 20-800°C. A heating rate of 20°C / min and a sample size of 10 ± 5mg were used in each experiment.

Perkin Elmer Pyris 6 differential scanning calorimeter (Walthan, MA) was used for the thermal characterization of polymers. DSC scans were recorded in a static air atmosphere at a heating rate of 10°C /min with 5±1 mg of samples.

3.4 Pour Point Measurement

The synthesized polymers were evaluated as PPDs with the base oil through pour point tests according to the ASTM D 97-93 standard method.[18] The polymers (at a concentration of 0.05 and 0.1 wt % of base oil) were added to the base oil I and II having pour point of -6°C and -15°C respectively and the mixtures were heated at 60°C for 2 h to dissolve the polymers in the base oil. A Lawler-Edison (New Jersey) pour point tester was used to measure the pour points of the prepared base oil mixtures. The prepared samples were maintained at 40°C for a given time and were then placed into testing vials. They were cooled in a cooling bath and the temperature was dropped by 1°C up to the pour point.

IV. RESULTS AND DISCUSSION

4.1 Characterization of PS/PLMA Random Copolymer
### (i) Molecular Weight Determination of PS/PLMA Copolymers

The molecular weight of poly(styrene-LMA) copolymer was determined by GPC. Figure 1.1 shows that molecular weight of copolymers increased with increase in percent conversion and Figure 1.2 shows that polydispersities are higher at the initial phase of polymerization that became lower at higher conversion.

(ii) Structural Characterization of Copolymer

Structural characterization of styrene/LMA copolymers was done by recording ^{1}H-NMR spectra in $CDCl_3$. Figure 1.3 show the ^{1}H-NMR spectra of these copolymers. In such copolymers, signals due to OCH_2 of LMA and aromatic protons of styrene were observed at δ= 3.9 ± 0.01 ppm and δ= 6.5-7.2 ppm respectively in the ^{1}H-NMR spectra of copolymers. The other characteristic proton signals were observed at δ=0.8-1.2 ppm (CH_3) and δ=1.8-2.0 ppm (CH_2 and CH group). The intensity of the signals due to aromatic protons increased with increasing amount of styrene in the copolymers.
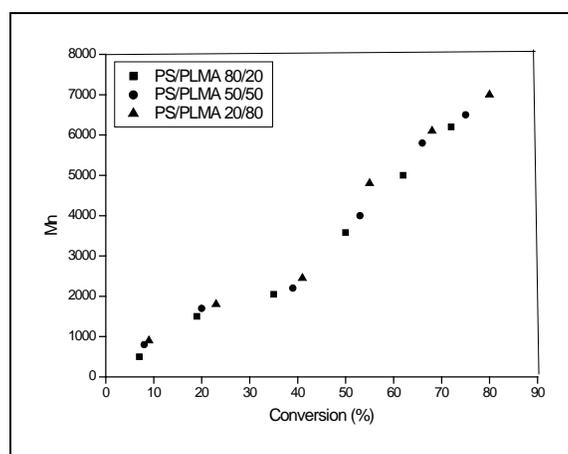
Figure.1.1: Plot of molecular weight (M_n) vs. conversion (%) in case of styrene/LMA copolymerization [Styrene/LMA: EBiB: OPMI=100: 1: 1: 2.5]
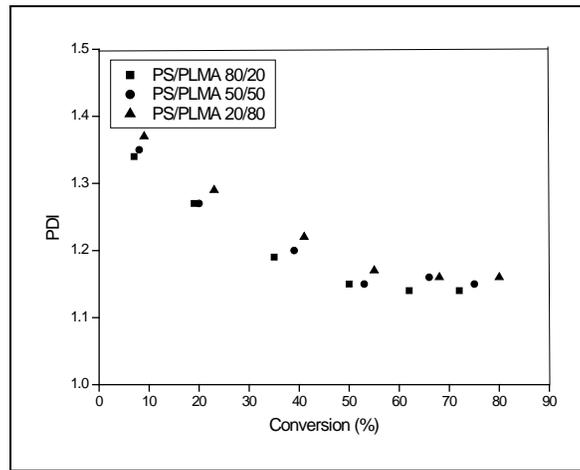
Figure 1.2: Plot of PDI vs. conversion (%) in case of styrene/LMA copolymerization. [Styrene/LMA: EBiB: OPMI=100: 1: 1: 2.5]

Since, the peak intensity correspond to the total number of protons in a particular group, the mole fraction of the monomer in a copolymer can be calculated using equation 1.1.

$$\frac{\text{Intensity of aromatic proton } (I_a)}{\text{Intensity of OCH}_2 \text{ of LMA } (I_b)} = \frac{5F_1}{2F_2} = \frac{5F_1}{2(1-F_1)} \quad (1.1)$$

Where F_1 is the mole fraction of styrene and F_2 is that of LMA. Equation 1.1 is based on the fact that LMA contains two protons in the OCH_2 and the styrene contains

five protons in the aromatic nucleus. Since $F_2 = (1-F_1)$, we get

$$F_1 = \frac{2 I_a}{5 I_m + 2 I_a} \quad (1.2)$$

From the intensities of NMR signals for aromatic proton of styrene and OCH_2 protons of LMA, the mole fraction of styrene in copolymers was calculated in accordance to equation 1.2. The results of copolymer composition thus determined are summarized in Table 1.2

Table.1.2: Copolymer composition data of the styrene/LMA copolymers ($_{< 15\%}$ conversion)

Sample Designation	mole fraction of styrene in feed [f_1]	mole fraction of styrene in copolymer [F_1]
PS/PLMA 80/20	0.80	0.74
PS/PLMA 60/40	0.60	0.54
PS/PLMA 50/50	0.50	0.46
PS/PLMA 40/60	0.40	0.39
PS/PLMA 20/80	0.20	0.22

(iii) Determination of Monomer Reactivity Ratio

Several methods have been reported in the literature for the evaluation of monomer reactivity ratios. However in the present work, reactivity ratios were calculated by computational method using Kelen-Tudos method and this was confirmed from nonlinear Error in Variable Model (EVM) program

The initial estimate of the reactivity ratios was done by the Kelen-Tudos method. The values of the terminal model reactivity ratios obtained from KT plot are $r_S = 0.56 (\pm 0.07)$, $r_{LMA} = 0.78 (\pm 0.08)$ respectively. These values along with the copolymer data were used to

calculate the reactivity ratio using the nonlinear Error in Variable Model (EVM) program. The values of reactivity ratios obtained from EVM method were $r_S = 0.53$, $r_{LMA} = 0.65$ respectively.

Then the mole fraction (F_1) of styrene monomer in the copolymer is plotted vs percent conversion. Variation of F_1 with percent conversion is shown in Figure 1.5 There is small compositional drift in the copolymer with increase in percent conversion. This is attributed to the fact that the reactivity of LMA is slightly higher than styrene.

4.2 Thermal Characterization

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Figure 1.5 (a-e) shows the TG/DTG traces of all copolymers. Three step degradation was observed in copolymers richer in LMA, whereas copolymer richer in styrene showed two and one step degradation. PLMA homopolymer showed two step degradation whereas in polystyrene homopolymers, one step degradation was observed The relative thermal stability of the copolymers was compared by comparing decomposition temperature at varying percent mass loss i. e. 10, 20 and 50% and the results are summarized in Table 1.3. These results clearly show that the degradation temperature at varying percent mass loss increased with increasing amount of styrene in copolymers.
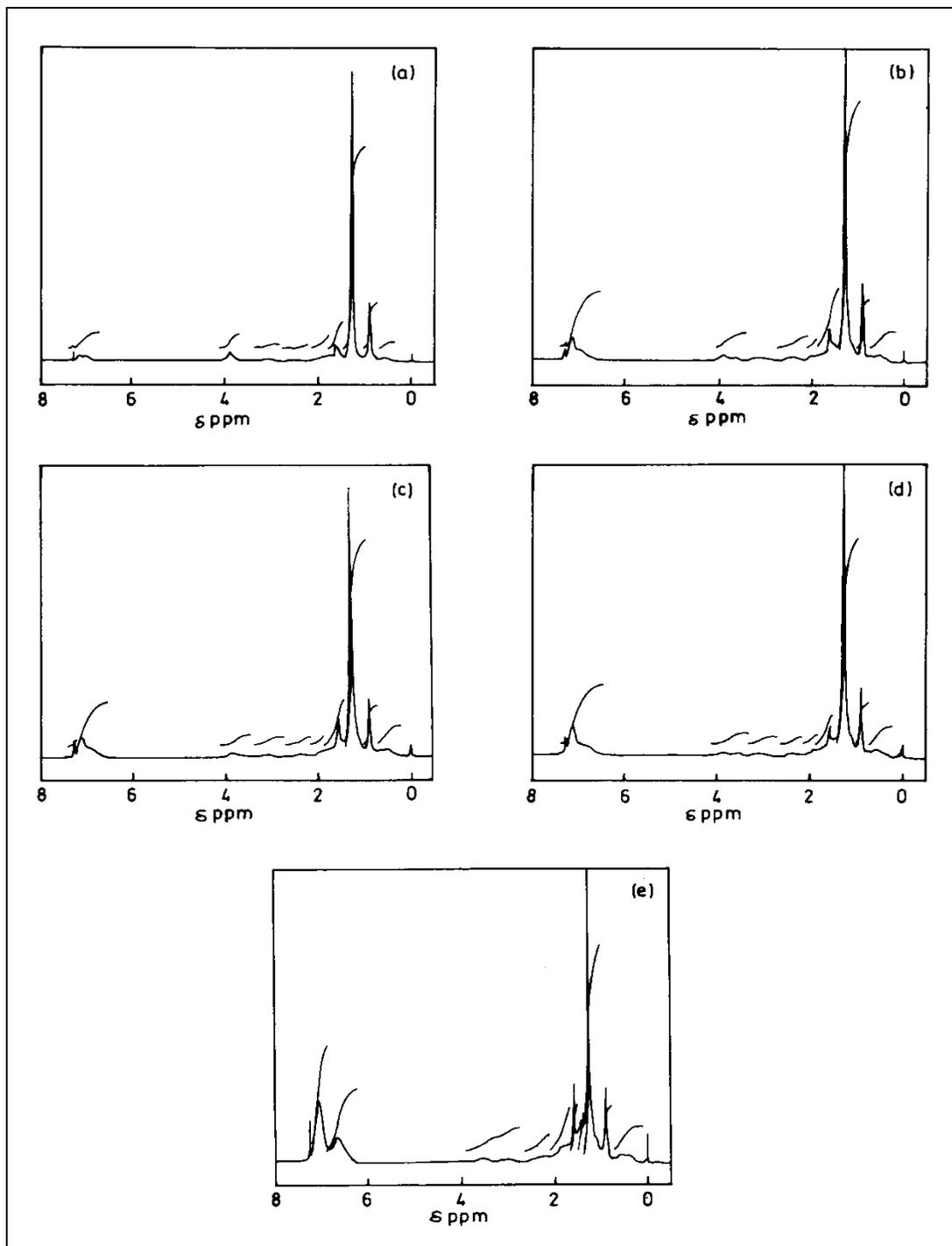
Figure.1.3: ^{1}H-NMR spectra of copolymers (a) PS/PLMA 20/80; (b) PS/PLMA 40/ 60; (c)PS/PLMA50/50; (d)PS/PLMA60/40; (e)PS/PLMA 80/20)
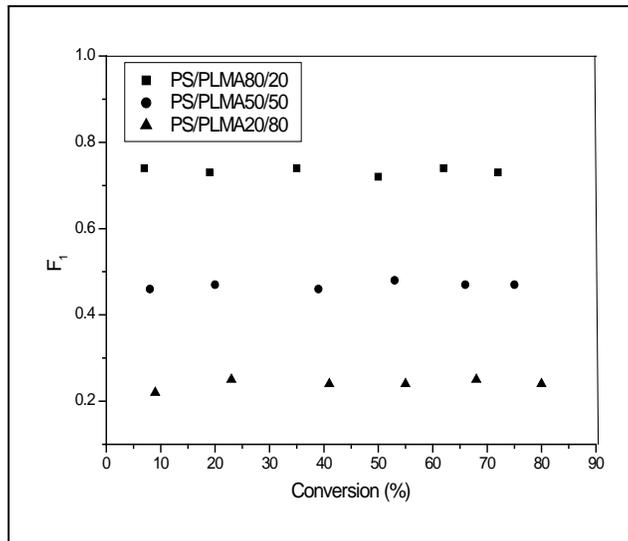
Figure.1.4: Plot of copolymer composition (F$_1$) vs conversion (%) as a function for styrene/LMA copolymers

Table 1.3: Results of TG/DTG traces for copolymers (styrene/ LMA copolymers) in N$_2$ atmosphere (Heating Rate 20°C /min)

| Sample Designation	T$_i$ (˚C)	T$_{max}$ (˚C)	T$_f$ (˚C)	Decomposition temperature (°C) at % mass loss of		
				10	20	50
PS/PLMA 20/80	221.6 279.7 349.5	242.9 306.7 390.4	267.0 326.5 424.6	241.8	269.7	347.6
PS/PLMA 40/60	219.4 280.9 354.3	240.9 311.9 401.4	267.8 330.6 429.2	250.4	288.4	364.4
PS/PLMA 50/50	240.5 358.5	301.0 408.9	358.5 443.1	263.8	298.4	380.0
PS/PLMA 60/40	258.8 364.3	315.7 412.7	320.9 447.4	287.8	337.0	397.4
PS/PLMA 80/20	401.4	418.2	451.7	387.8	401.3	418.0
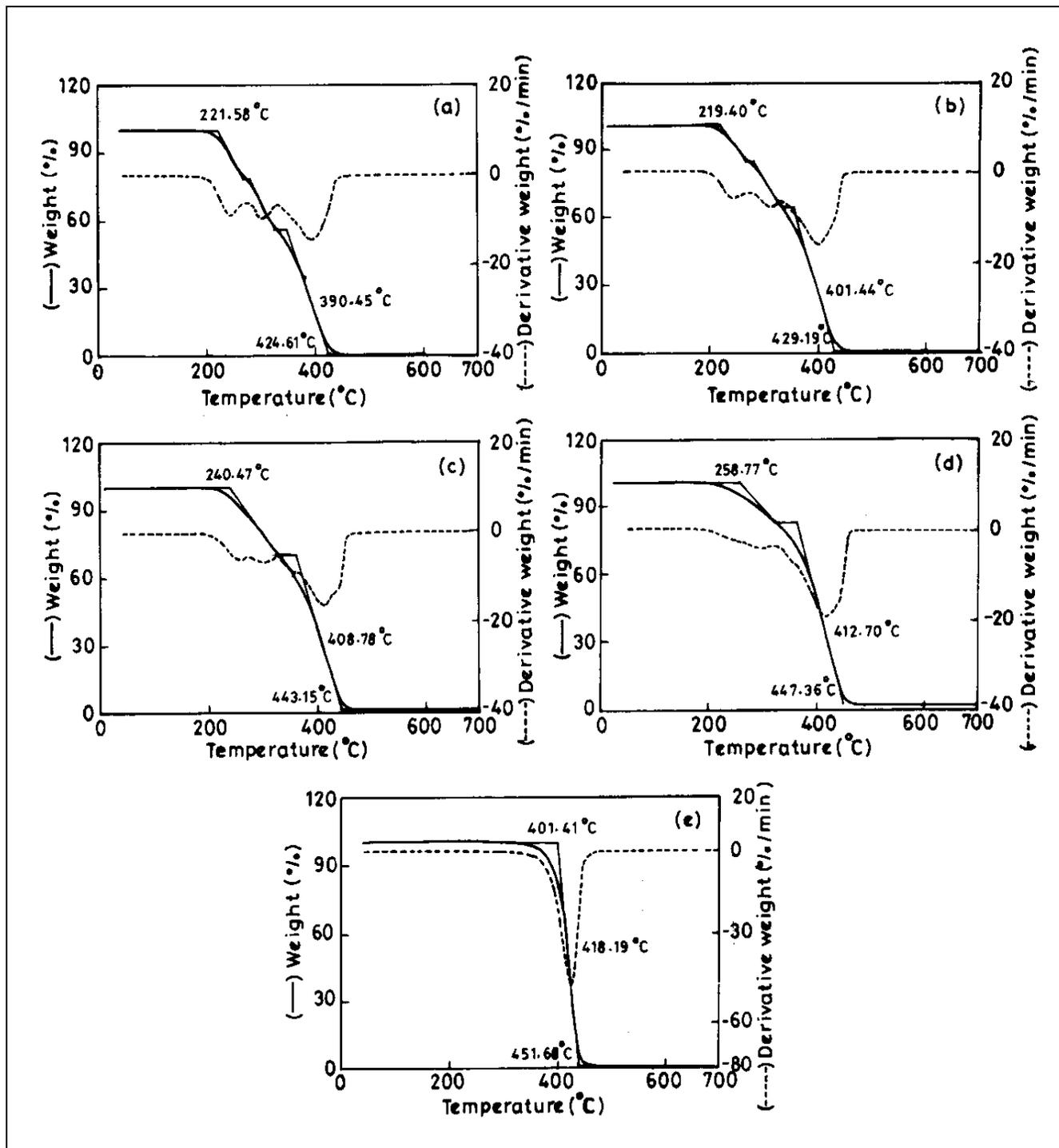
Figure 1.5: *TG/DTG traces of styrene/LMA copolymers* (a) PS/PLMA 20:80,(b)PS/PLMA40:60, (c)PS/PLMA60:40, (d)PS/PLMA 60:40 and (e) PS/PLMA80:20

4.3 DSC Studies

In order to investigate the effect of copolymer composition on the glass transition, DSC scans of various copolymers were recorded. Figure 1.6 show the DSC scans of copolymers. An endothermic shift in base line corresponding to the glass transition temperature was observed in all the samples. In the first heating cycle, an endothermic peak was observed in most of the samples which may be due to the bulk stress relaxation. In order to have a same thermal history, the samples were first heated in a DSC cell from 50-150°C followed by cooling in the DSC cell to room temperature. The same samples were reheated from -70 to 150°C at a heating rate of 10°C / min to record the DSC traces. The second heating scans were

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used in all the copolymer samples for characterizing glass transition region and the results are summarized in Table

1.4 Tg values for a random copolymer can also be predicted using Fox equation [1.3].

$$\frac{1}{Tg} = \frac{w_1}{Tg_1} + \frac{w_2}{Tg_2} \qquad (1.3)$$

Where Tg_1 and Tg_2 represents the Tg of homopolymers [polystyrene and PLMA] and w_1 and w_2 represents their weight fractions. Tg was also calculated using Fox equation and the results are summarized in

Table 1.4 Tg values for the copolymers calculated using Fox equation[19] was in good agreement with the experimental values obtained from the DSC traces.

Table.1.4: Glass transition temperature of copolymers

Sample Designation	Tg (^{o}C) (Experimental)	Tg (^{o}C) (Calculated by Fox equation)
PS/PLMA 80/20	68.83	70.82
PS/PLMA 60/40	29.16	30.03
PS/PLMA50/50	20.11	21.16
PS/PLMA40/60	12.02	12.71
PS/PLMA20/80	-16.99	-16.88
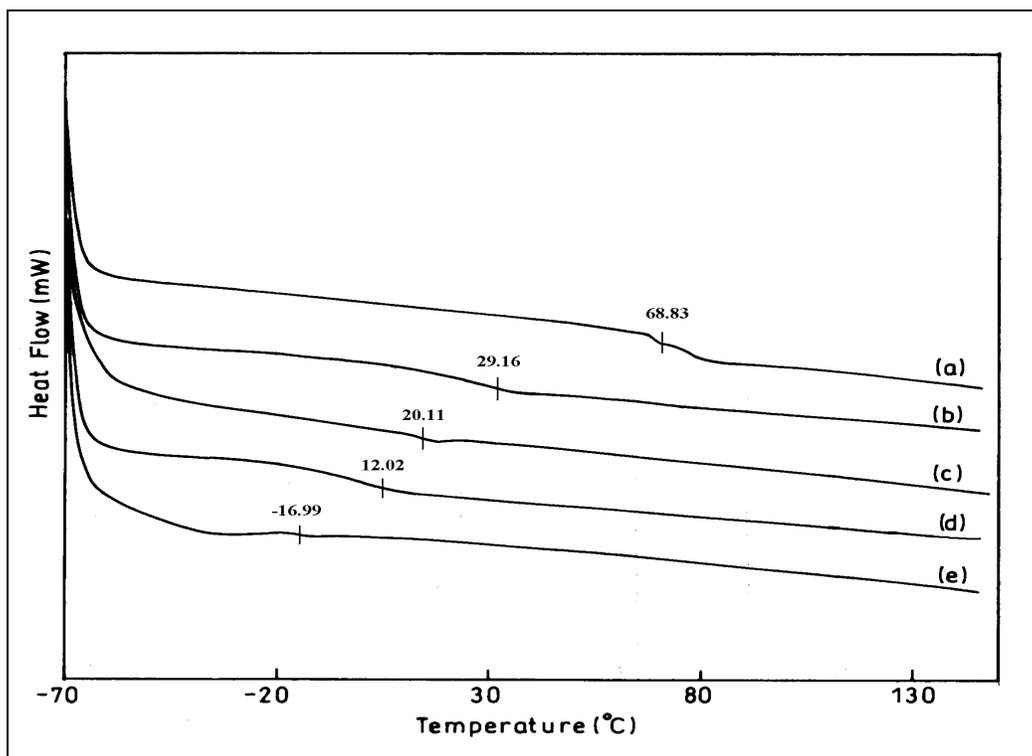
Figure 1.6: DSC traces of styrene/LMA copolymers (a) PS/PLMA 80/20 (b) PS/PLMA 60/40 (c) PS/PLMA50/50 (d) PS/PLMA40/60 (e) PS/PLMA20/80

4.4 Evaluation of Copolymers as Pour Point Depressant

The base oil, which had a Saybolt universal second of 150 was used for the pour point experiments. The experiments were performed at least three times and each mixture to be measured contained the base oil and polymer at a concentration of 0.05 wt % and 0.1 wt %. The average values of the pour points are listed in Table 1.5

and 1.6. The pour points of the pure base oil I and II was-6°C and -15°C.

The pour point values of few samples decreased relative to that of the pure base oil. The effects of PPD properties of homopolymer of LMA are higher than copolymer. It was observed from the Table 1.5 and 1.6 that the entire sample shows maximum decrease in the case of base oil having higher pour point e.g.-6°C than the base oil

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having lower pour point e. g.-15°C. It was also observed from the Table 1.5 and 1.6 that as the styrene content increases in the copolymers, there is no change in the pour point of base oil the reason for that could be as the styrene content in the copolymers increases the solubility of copolymers in the base oil deceases.

Table.1.5: Pour Point Depressant (PPDs) Properties in Base Oil I (-6°C) as per ASTM D97-93

Sample Designation	0.05Wt%	0.1Wt%
PS/PLMA 80/20	-6	-6
PS/PLMA 60/40	-6	-6
PS/PLMA 50/50	-6	-7
PS/PLMA 40/60	-8	-8
PS/PLMA 20/80	-8	-9
PLMA	-10	-13

Table.1.6: Pour Point Depressants (PPDs) Properties in Base Oil II (-15°C) as per ASTM D97-93

Sample Designation	0.05Wt%	0.1Wt%
PS/PLMA 80/20	-15	-15
PS/PLMA 60/40	-15	-15
PS/PLMA 50/50	-15	-15
PS/PLMA 40/60	-15	-15
PS/PLMA 20/80	-16	-18
PLMA	-18	-20

V.   CONCLUSION

Series of styrene/LMA copolymers were synthesized via ATRP method which shows the good control of polymerization. The copolymer composition data obtained from ^{1}H-NMR spectra have been used to determine reactivity ratios. The reactivity ratios obtained from EVM method $r_S = 0.53$, $r_{LMA} = 0.65$ were in good agreement with the values calculated using Kelen-Tudos method. Although the thermal stability of the copolymer increased with increasing amount of styrene in copolymer but it decreases the solubility of the copolymers in the base oil and copolymers with higher styrene content shows low PPDs properties.

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