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FREE RADICAL-INITIATED COPOLYMERIZATION OF 2,6-DICHLOROSTYRENE WITH MALEIMIDE, N-METHYLMALEIMIDE, AND N-PHENYLMALEIMIDE

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Key Words: 2,6-Dichlorostyrene, Poly(2,6-dichlorostyrene-co-maleimide), Poly (2,6-dichlorostyrene-co-N-methylmaleimide), Poly(2,6-dichlorostyrene-co-N-phenylmaleimide), Mechanism of Copolymerization, Reactivity Ratios, Thermal Properties

ABSTRACT

The free-radical-initiated copolymerization of 2,6-dichlorostyrene (2,6-DClSt), with maleimide (MI), N-methylmaleimide (NMeMI) and N-phenylmaleimide (NPhMI) was carried out in butanone or in toluene at 65°C with different monomer-to-monomer ratios in the feed. The copolymer composition was evaluated by chlorine content in polymers. The reactivity ratios determined by Kelen-Tüdös method indicate the random arrangement of monomers in copolymer chains. In all studied systems, azeotropic points were observed at ratios of: 0.5 (2,6-DClSt) to 0.5 (MI) and 0.4 (2,6-DClSt) to 0.6 (NMeMI and NPhMI). Molecular weights of copolymer, which contain equimolar ratio of 2,6-DClSt-co-MI, NMeMI, and NPhMI are: $M_w \cdot 10^{-3} = 46.1; 90.4; 81.4$. $M_n 10^{-3} = 27.1; 46.0; 37.0$. The copoly-

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mers are thermostable, film forming materials, which decompose by one-step mechanism between 400°C, and 500°C.

The T_g's are linearly distributed between T_g's of homopolymers and in all cases, single well defined T_g's are obtained.

INTRODUCTION

In the previous papers from our laboratories, it was shown that maleimide (MI), N-methylmaleimide (NMeMI) and N-phenylmaleimide (NPhMI) copolymerize with α-methylstyrene yielding alternating copolymers regardless of the ratio of comonomers in the feed. In all cases, the copolymerization proceeds via the charge-transfer complex mechanism [1-4]. By applying similar experimental conditions, we have performed the copolymerization of 2,6-DClSt with MI, NMeMI and NPhMI. The results of these studies are the subject of the present paper.

EXPERIMENTAL

Chemicals

2,6-Dichlorostyrene was a commercial product of 99% purity (Aldrich Europe). A freshly distilled fraction boiling at 98°C at 1.04 kPa (8 mm Hg) was used in the copolymerization procedure. MI of 99% purity (Aldrich Europe) was recrystallized from $CHCl_3$; mp. 93-94°C; NMeMI and NPhMI were commercial products (Aldrich Europe) and were used without subsequent purification.

Physicochemical Measurements

NMR spectra were obtained on a Varian EM 390 spectrometer. The copolymer composition was determined by elemental analysis. Molecular weights were determined on a Varian HPGPC Model 5800 using a set of Styragel columns in THF as solvent. Differential scanning calorimetry was carried out on a Perkin-Elmer model DSC-2 with a scanning rate of 20°C/min. The thermograv-imetric analysis was carried out on a Perkin-Elmer TGS-2 thermogravimetric system in nitrogen stream with heating rate of 10°C/min.

Copolymerization Procedure

Copolymerization was performed in 10 mL glass vials, thoroughly degassed, filled with nitrogen before sealing and placed into a thermostated oil bath. The volume of reaction mixture was 2 mL in butanone at a total monomer concentration of 2 mol L^{-1}. Copolymerization reactions were initiated with 0.5 wt% of AIBN at 65°C. The viscous solution of polymers was diluted with chloroform and precipitated by dropwise addition of methanol. The polymer was filtered off and dried in vacuum at 80°C overnight. Composition of copolymers was determined from the chlorine content. Poly(2,6-DClSt) was prepared in toluene at 70°C with 0.5 wt% of AIBN.

RESULTS AND DISCUSSION

The interest in the use of chlorinated polystyrene derivatives stems from the fact that these polymers and copolymers have higher thermal stability and lower flammability than the non-chlorinated derivatives. 2,6-Dichloro-styrene was prepared by Marvel and coworkers [5] in 1946 from 2,6-dichloro-benzaldehyde which was converted to the corresponding carbinol by Grignard reaction, followed by dehydration. Monomer 2,6-DClSt was homopolymerized by the same authors by initiation with ultraviolet light.

As far as we know, the copolymerization of 2,6-DClSt was published so far only by Aggarwal and Long in 1952 [6] and by Huglin and Yip in 1988 [7]. In the first cited paper [6], a mixture of dichlorostyrenes containing less than 10% of 2,6-DClSt was copolymerized with 2-vinylpyridine and with methyl acrylate, while in the second paper [7], some observations on the copolymerization of 2,6-DClSt with N-vinyl-2-pyrrolidone are described.

In the present paper, the preparation of copolymers of 2,6-DClSt with MI, NMeMI and NPhMI are described. On admixture of 2,6-DClSt with MI, NMeMI or NPhMI no change of color was observed and by applying the transformed Benesi-Hildebrand NMR procedure [8, 9] it was found that there was no change of chemical shifts when the concentration of 2,6-DClSt was increased in the mixture, thus indicating that the charge-transfer complex was not formed.

Polymerization conditions and properties of the prepared copolymers are described in Tables 1, 2, and 3.

The copolymerization diagram for all three copolymerization systems presented in Figure 1 indicates that the copolymerization proceeds statistically

TABLE 1. Polymerization Conditions and Properties of Poly(2,6-DClSt-co-MI)[a]

Molar fraction of 2,6-DClSt in feed	Molar fraction of 2,6-DClSt in copolym.	Time (min)	Conversion (%)	Cl_2 (%)	T_g (°C)	Molecular weight $M_w \cdot 10^{-3}$	Molecular weight $M_n \cdot 10^{-3}$	Weight loss (%) 400°C	Weight loss (%) 450°C	Weight loss (%) 500°C
0.2	0.29	170	22.48	17.41	343	43.1	31.1	0.3	36.5	78.3
0.3	0.35	220	29.41	20.37	325	43.0	27.9	0.5	43.5	80.1
0.4	0.43	220	24.13	23.65	313	50.9	31.6	0.5	52.0	85.1
0.5	0.49	240	23.77	25.93	303	46.1	27.1	0.6	73.0	89.0
0.6	0.56	330	26.65	29.16	289	47.0	25.1	1.7	80.0	91.4
0.7	0.60	360	21.72	28.22	278	54.2	26.0	2.0	75.0	95.0
0.8	0.67	390	15.38	32.51	257	46.0	22.5	6.5	86.2	98.0

[a] Molecular weight of poly(2,6-DClSt): $M_w \cdot 10^{-3} = 39.0$; $M_n \cdot 10^{-3} = 18.1$

with azeotropic points at a molar ratio of 0.5 (2,6-DClSt) to 0.5 (MI), and at molar ratio of 0.4 (2,6-DClSt) to 0.6 (NMeMI and NPhMI).

Figure 2 represents the plot of initial rate of copolymerization of 2,6-DClSt with MI, NMeMI and NPhMI versus the molar ratio of 2,6-DClSt in the monomer feed. It is evident that by increasing the amount of 2,6-DClSt in the

TABLE 2. Polymerization Conditions and Properties of Poly(2,6-DClSt-co-NMeMI)

Molar fraction of 2,6-DClSt in feed	Molar fraction of 2,6-DClSt in copolym.	Time (min)	Conversion (%)	Cl_2 (%)	T_g (°C)	Molecular weight $M_w \cdot 10^{-3}$	Molecular weight $M_n \cdot 10^{-3}$	Weight loss (%) 400°C	Weight loss (%) 450°C	Weight loss (%) 500°C
0.2	0.30	60	19.67	16.30	271	120.0	63.6	1.0	65.5	96.7
0.3	0.34	100	30.78	18.52	264	102.3	55.2	1.2	60.0	97.0
0.4	0.40	180	40.84	20.97	257	104.6	56.3	1.2	55.0	96.6
0.5	0.44	180	37.15	22.63	250	102.6	53.8	1.1	56.8	97.7
0.6	0.48	180	28.02	24.24	245	90.4	46.0	1.5	55.0	97.0
0.7	0.52	240	29.19	26.11	237	80.8	42.3	2.7	73.0	97.0
0.8	0.57	257	22.22	27.89	229	60.4	29.5	3.0	65.5	97.4

TABLE 3. Polymerization Conditions and Properties of Poly(2,6-DClSt-co-NPhMI)

Molar fraction of 2,6-DClSt		Time (min)	Conversion (%)	Cl_2 (%)	T_g (°C)	Molecular weight		Weight loss (%)		
in feed	in copolym.					$M_w \cdot 10^{-3}$	$M_n \cdot 10^{-3}$	400°C	450°C	500°C
0.2	0.25	200	54.29	10.27	297	81.4	38.4	1.1	72.3	85.5
0.3	0.33	240	56.24	13.06	283	81.6	39.1	2.1	85.0	91.8
0.4	0.40	240	52.31	16.48	268	86.8	45.3	2.6	81.5	94.2
0.5	0.47	240	48.44	19.30	263	89.2	48.2	3.0	82.0	93.4
0.6	0.52	360	53.40	21.14	257	81.4	37.0	5.2	84.0	95.1
0.7	0.54	360	34.83	22.28	249	78.4	33.4	5.3	76.1	95.4
0.8	0.60	360	29.48	24.55	240	46.4	23.7	7.4	79.5	96.8

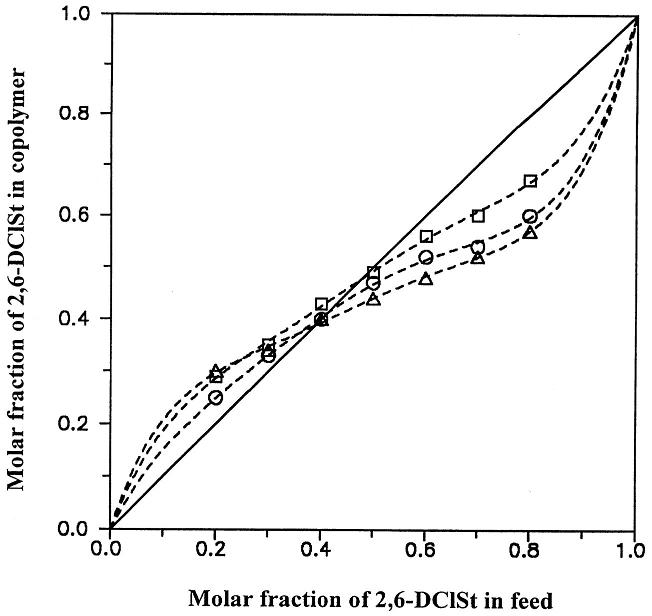

Figure 1. Ratio of molar fraction of 2,6-DClSt in feed and in copolymer with MI (□), NMeMI (Δ) and NPhMI (○).

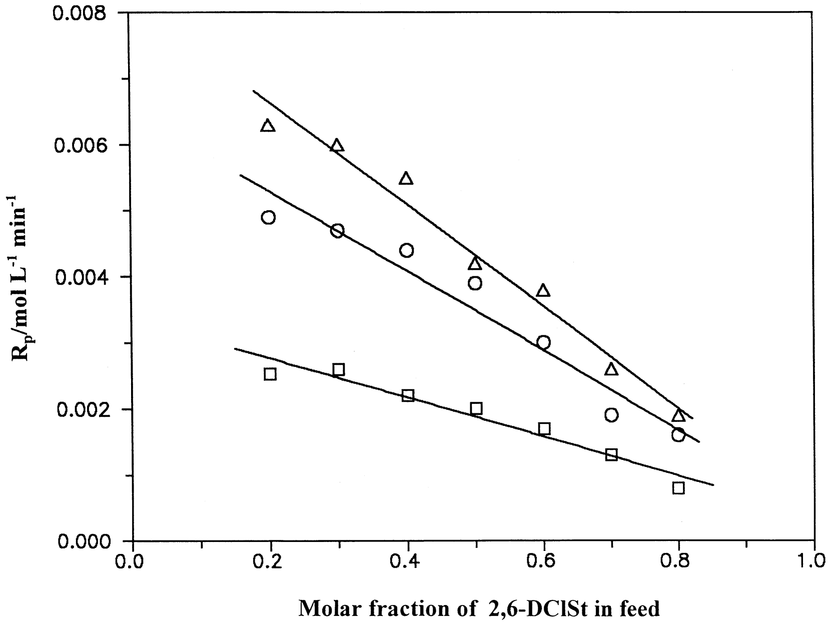

Figure 2. Initial copolymerization rates versus monomer feed molar ratios in the copolymerization of 2,6-DClSt with MI, NMeMI and NPhMI in buta-none; 0.5% AIBN at 65°C; total monomer concentration 2.0 mol L^{-1}.

feed, the initial rate of copolymerization decreases. The same was also found in many other copolymerization reactions of donor-acceptor monomers studied in our laboratories [10, 11].

The reactivity ratios in the copolymerization were determined graphically with Kelen-Tüdös Equation 1 (Figure 3):

$$\eta = \left(\frac{r_1 + r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha} \qquad (1)$$

where η and ξ are functions of the molar fractions of monomers in the co-polymerization and in the feed respectively, and α is an arbitrary parameter [12].

Numerical values of the reactivity ratios determined from the Figure 3, using the least-square method are:

r_1(2,6-DClSt) = 0.38; r_2 (MI) = 0.41; α = 1.0986
r_1(2,6-DClSt) = 0.12; r_2(NMeMI) = 0.44; α = 1.3439
r_1(2,6-DClSt) = 0.21; r_2(NPhMI) = 0.54; α = 1.5428

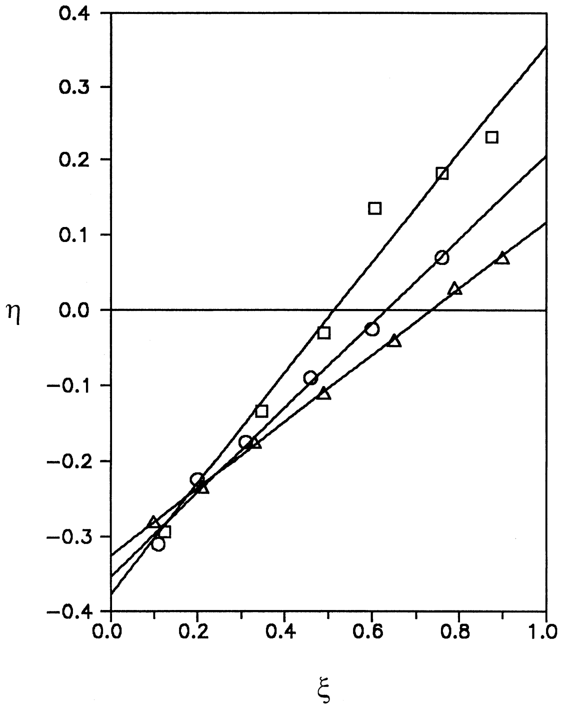

Figure 3. Kelen-Tüdös diagram for calculation of reactivity ratios in copolymerization of 2,6-DClSt with MI, NMeMI and NPhMI.

The copolymers studied in this paper belong to the comb-like polymers, which are often characterized by high temperature stability and regular domains within the amorphous polymer matrix. For this reason it is of interest to study the thermal properties of copolymers of 2,6-DClSt with MI, NMeMI, and NPhMI. As evident from Tables 1-3, all studied copolymers are stable at temperatures up to 400°C under the thermogravimetric conditions and have Tg's within the thermostable region of polymers.

Figure 4 illustrates the thermograms of copolymers prepared at molar ratios of 0.2 mole of 2,6-DClSt to 0.8 mol of maleimide derivatives and 0.8 mol of 2,6-DClSt to 0.2 mole of maleimide derivatives in feed. It is evident that copolymers decompose by one-step mechanism and that the thermal stability of all three copolymer systems decreases by the increase of 2,6-DClSt in the feed.

The comparison of thermal degradation of poly-2,6-DClSt and copolymers which contain equimolar amount of comonomers are shown in Figure 5. It is evident that all copolymers similarly decompose under the conditions of ther-

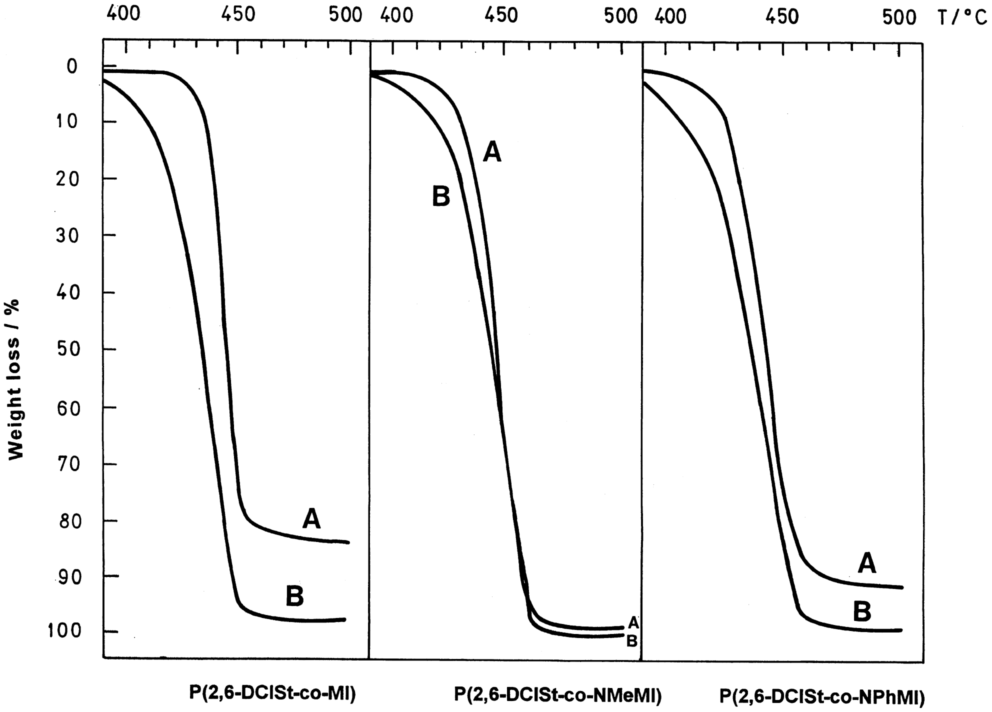

Figure 4. Thermograms of poly[2,6-DClSt-co-MI (NMeMI and NPhMI)] at molar ratios of comonomers in feed: 1) 0.2 mole of 2,6-DClSt to 0.8 mole of maleimide comonomers (A); 2) 0.8 mole of 2,6-DClSt to 0.2 mole of maleimide comonomers (B).

mogravimetric analysis, and that poly(2,6-DClSt-co-NMeMI) is somewhat more stable.

Numerical data of initial decomposition temperature (T_i), final decomposition temperature (T_f) and the temperature of maximal rate of weight loss (T_{max}) are calculated according to the procedure described by Jiang and coworkers [13]. Numerical data of thermogravimetric analysis and graphical illustration of the relationship between the temperature of maximal weight loss (T_{max}) and molar fraction of 2,6-DClSt in copolymers are presented in Table 4 and Figure 6. The data in Figure 6 indicate that T_{max} of copolymers poly(2,6-DClSt-co-NMeMI) and poly(2,6-DClSt-co-NPhMI) are not dependent on the molar fraction of 2,6-DClSt in copolymers, while the T_{max} of poly(2,6-DClSt-co-MI) decreases with the increase of the amount of 2,6-DClSt in copolymers.

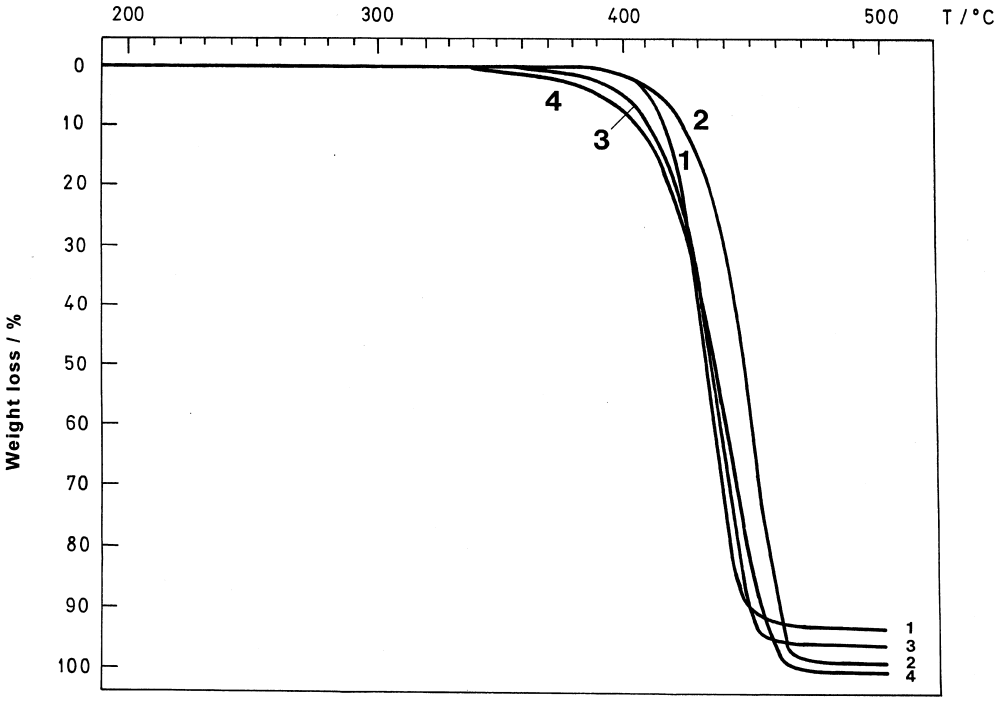

Figure 5. Thermograms of poly(2,6-DClSt) (1) and copolymers of 2,6-DClSt with MI (2), NMeMI (3) and NPhMI (4) at equimolar ratio of monomers in copolymer chains.

TABLE 4. Initial (T_i) and Final (T_f) Degradation Temperature and Maximal Rate of Degradation (T_{max}) of Copolymers of 2.6-DClSt with MI, NMeMI, and NphMI

Molar fraction of 2,6-DClSt in copolymer			T_i (^{0}C)			T_{max} (^{0}C)			T_f (^{0}C)		
MI	NMeMI	NPhMI	MI	NMeMI	NPhMI	MI	NMeMI	NPhMI	MI	NMeMI	NPhMI
0.29	0.30	0.25	434	435	424	443	447	438	451	458	453
0.35	0.34	0.33	428	433	420	440	448	435	450	463	350
0.43	0.40	0.40	426	431	420	438	449	437	451	466	453
0.49	0.44	0.47	420	432	419	432	449	437	444	464	453
0.56	0.48	0.52	417	434	416	431	449	436	445	464	454
0.60	0.52	0.54	414	426	418	428	447	437	443	460	458
0.67	0.57	0.60	414	428	415	428	448	437	450	463	458

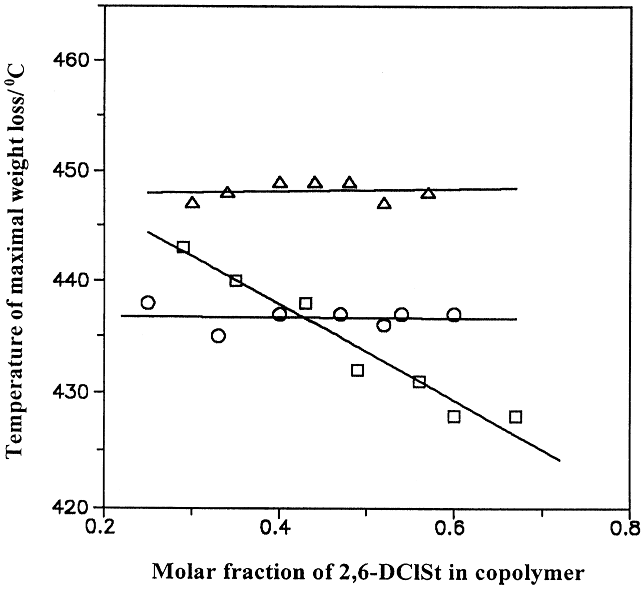

Figure 6. Relationship between molar fraction of 2,6-DClSt in copolymers with MI (□), NMeMI (Δ) and NPhMI (○), and temperature of maximal rate of weight loss under the DTA conditions.

During the course of our previous studies on the thermal properties of comb-like homopolymers and copolymers based on electron donor-acceptor monomers it was found that beside the T_g's, some of these polymers show the higher transition temperatures in mesophase, thus indicating the possibility of existence of regular domains in amorphous phase [11], [14-16]. In continuation of our studies in the present paper is shown that the T_g's of all studied copolymers occur at relatively high temperature so that transitions at higher temperatures could not be observed.

The relationship between T_g's of copolymers of 2,6-DClSt with MI, NMeMI and NPhMI and molar ratio of comonomers in the copolymer chains is shown in Figure 7.

It is evident that T_g's are linearly distributed between T_g's of homopolymers, yielding single well defined first order transitions. The glass transition temperature of poly-MI was graphically determined to be about 416°C. In a previous paper we were not able to determine experimentally T_g of poly-MI since it decomposes on heating above 330°C without any indication of T_g [17].

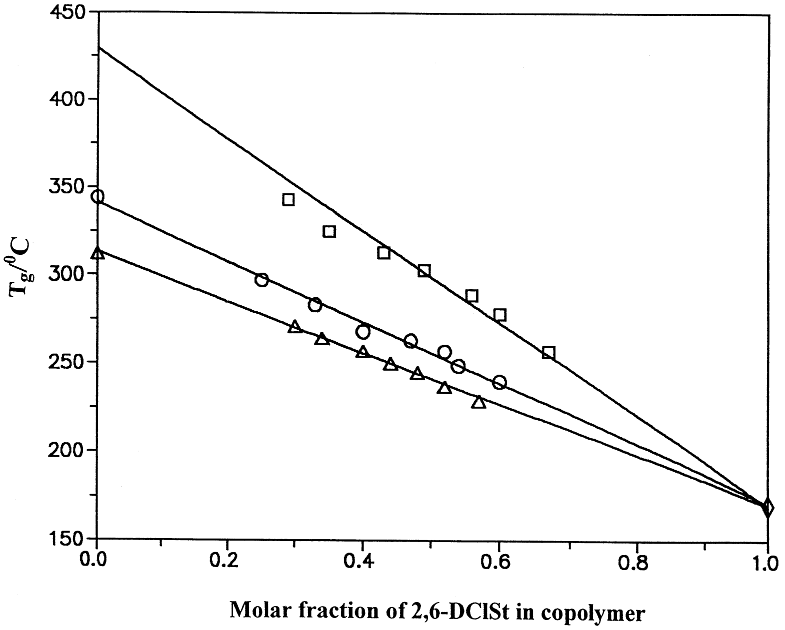

Figure 7. Relationship between T_g's of copolymers of 2,6-DClSt with MI (□), NMeMI (Δ) and NPhMI (○) and molar fraction of 2,6-DClSt in copolymers.

CONCLUSION

Copolymerization of 2,6-DClSt with MI, NMeMI and NPhMI was performed in butanone in the presence of AIBN, and it was found that the copolymerization is a statistical reaction with azeotropic composition at molar ratios of: 0.5 (2,6-DClSt) to 0.5 (MI) and 0.4 (2,6-DClSt) to 0.6 (NMeMI and NPhMI). Reactivity ratios for all three copolymer systems are lower than 1. All copolymers decompose under the DTA conditions by one-step mechanism with maximal rate of decomposition between 420-450°C. Glass transition temperatures of copolymers are within the thermally stable region and increase by the increase of molar fraction of maleimide comonomers.

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