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Copolymerization of α-methylstyrene with *N*-alkylmaleimides

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Dedicated to Professor Dragutin Fleš on the occasion of his 70th birthday

SUMMARY

Alternating copolymers of α-methylstyrene (α-MeSt) with N-alkylmaleimides (RMI; R=Et, n-Pr, iso-Pr, n-Bu, n-Hex) were prepared in Calvet differential microcalorimeter under different monomer-to-monomer ratios in the feed using AIBN as initiator. The equilibrium constants of CT-complex monomers have low values: 0.02 - 0.05 L.mol^{-1} but the mechanism of copolymerization indicates the participation of CT-complex. Equilibrium constants and rate of decomposition under the TGA conditions are not dependent on steric factors, but the rate of copolymerization decreases with the increase of bulkiness of alkyl substituent. In high conversion copolymerization it was observed that in the presence of an excess of homopolymerizable RMI, alternating copolymers are quantitatively formed prior to the formation of poly(RMI).

INTRODUCTION

In our previous papers it was shown that α-methylstyrene (α-MeSt) readily copolymerizes with N-phenylmaleimide (1), N-methylmaleimide (2) and maleimide (3) yielding alternating copolymers under various monomer-to-monomer ratios in the feed. It was further shown that in high conversion copolymerization with an excess of homopolymerizable electron acceptor the homopolymerization is preceded by copolymerization. In continuation of this work, the copolymerization of α-MeSt with N-alkylmaleimides (RMI; R=Et, n-Pr, iso-Pr, n-Bu, n-Hex) was performed and the influence of steric factors on the mechanism of copolymerization was studied.

EXPERIMENTAL

Materials

α-MeSt was commercial product (Aldrich Europe, Belgium), 99% purity; fraction boiling at 50^{o}C/1.3 kPa was used; EtMI (Aldrich Europe, Belgium) was used without purification; RMI (R=n-Pr, iso-Pr, n-Bu, n-Hex) (Table 1) were prepared by slightly modified method described by Mehta et al. (4) as examplified in the preparation of iso-PrMI: Isopropylmaleamic acid (iso-PrM acid) was prepared in 85% yield from 20 g (0,2 mol) MAn in 50 ml of $CHCl_3$ and 11.8 g (17.1 ml., 0,2 mol) of iso-$PrNH_2$ in 25 ml $CHCl_3$ following procedure by Mehta et al. (4). Iso-PrM acid (26 g., 0.17 mol)

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40 ml acetic anhydride and 4 g. of sodium acetate heated for 1 hr on a steambath at 100^{o}C under stirring with a magnetic stirrer. After cooling, the reaction mixture was poured into ice water and stirred for 2 hrs. The equeous mixture was extracted with four 40-ml portions of Et_2O, the Et_2O layer was neutralized with a 10% solution of Na_2CO_3 and dried with Na_2SO_4 overnight. Ether was removed and the residue (16.4 g) was distilled at 105-108^{o}C at 1.8 kPa yielding 8 g (35%) of colorless oil; m.p. 21-22^{o}C. The properties of RMI are shown in Table 1.

Physicochemical Measurements

The equilibrium constants of CT-complexes were determined by the NMR continuous variation method in $CDCl_3$ at 35^{o}C (5,6). Differential scanning calorimetry was carried out on a Perkin-Elmer Model DSC-2, using scanning rate of 20^{o}C/min in nitrogen with a sample size of 15 mg. The only distinctive feature of the DSC thermograms was T_g. Thermal stability of copolymers was determined on a Perkin-Elmer TGS-2 Thermogravimetric System in the temperature range of 50-500 F. Molecular weights were determined on a Varian HPGPC Model 5800 using a set of 4 Styrogel columns with THF as solvent. The average molecular weights were calculated by calibration with standard polystyrene of known molecular weights.

RESULTS AND DISCUSSION

The data in Table 2 indicate that α-MeSt forms with RMI (R=Et, n-Pr, iso-Pr, n-Bu, n-Hex) CT-complex with very low complexation constants: 0.03 to 0,06 L.mol^{-1}. The same was also found in the complexation of α -MeSt with PhMI (K=0.03 L.mol^{-1}) and with MeMI (K=0.02 L.mol^{-1}). Obviously steric factors have no influence on the complexation constant, thus indicating that the complexation is formed through the vinyl bonds similar to the complexation of phenylvinyl alkyl ethers (PhVAE) with maleic anhydride (MAn) where complexation constants were for an order of magnitude higher than in the case of α-MeSt/RMI (7).

Table 1. Properties of N-alkylmaleimides (RMI)

R	M.P./C^{o}C	B.P./^{o}C 1.8 kPa	Yield/%	%,C,H,N					
				Found			Calc'd		
				C	H	N	C	H	N
n-Pr	27-29	110-115	46.5	60.58;	6.52;	9.35	60.41;	6.52;	10.07
iso-Pr	21-22	105-108	35.0	59.93;	6.40;	9.89	60.41;	6.52;	10.07
n-Bu	10	120-122	39.1	62.09;	7.13;	9.05	62.72;	7.34;	9.15
n-Hex	24-25	130-133	50.5	65.82;	8.62;	7.98	66.27;	8.34;	7.73

Polymerization Procedure

Polymerizations were performed homogeneously in $CHCl_3$ as solvent to high conversion in differential microcalorimeter Calvet Setaram Instruments, Lyon, France at 60^{o}C in the presence of 0.3 wt/% of AIBN. The reaction mixture was diluted with $CHCl_3$ and poured into methanol. The precipitate was filtered off, washed with cold methanol and dried in vacuo overnight at 70^{o}C. Properties of α-MeSt/RMI copolymers are presented in Table 2.

Table 2. Properties of poly(-MeSt-alt-RMI)

R	10^3R_p [a] $mol.L^{-1}min^{-1}$	T_g/K	M_w $g.mol^{-1}$	M_n $g.mol^{-1}$	K [b] $L.mol^{-1}$	wt loss/°C 10	 50	 90
Et	2.36	462	52 700	22 900	0.05	323	368	389
n-Pr	1.66	454	41 200	19 000	0.03	333	368	389
iso-Pr	0.58	485	34 200	18 100	0.03	336	370	389
n-Bu	1.34	410	52 300	25 200	0.04	330	370	394
n-Hex	2.09	382	70 800	25 300	0.06	330	371	401

[a] Total monomer concentration 2 $mol.L^{-1}$
[b] Equilibrium constants of CT-complex monomers

As previously shown the equilibrium constants of CT-complexes were not significantly dependent on steric factors but the rate of copolymerizations of α-MeSt with RMI was largely influenced by the bulkiness of alkyl groups as shown in Figure 1, where a plot of initial rate of conversion against molar ratio of comonomers is presented.

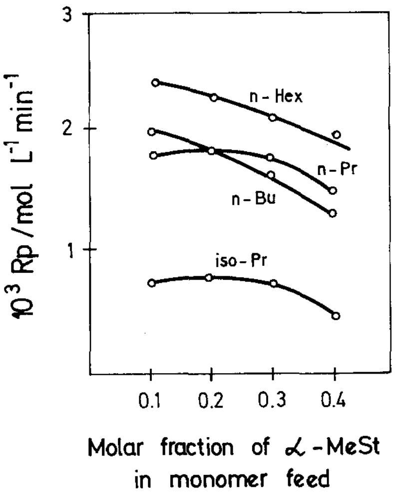

Figure 1. Initial copolymerization rates versus monomer feed molar ratios in copolymerization of α-MeSt with n-PrMI, n-BuMI, n-Hex, and iso-PrMI; 60°C in $CHCl_3$; 0.3 /% AIBN; total monomer concentration 2 $mol.L^{-1}$.

Alternating copolymers presented in Table 2 are thermostable compounds which decompose via a one step reaction as shown in Figure 2. It is of interest to note that there is no significant influence of steric factors on the thermal decomposition under the TGA conditions in nitrogen, while thermal decomposition of poly(PhVAE-alt-MAn) was a sterically controlled reaction (8). The glass transition temperature (T_g) of poly(α-MeSt-alt-RMI) indicates that $T_g$decreases when a higher alkyl chain was introduced in electron-acceptor monomers: R, T_g/K: Et, 462; n-Pr, 454; n-Bu, 416; n-Hex, 382. This is in agreement with values reported for homopolymers of N-alkylmaleimides (9,10). As expected the alternating copolymer of α-MeSt with iso-PrMI has the highest T_g = 485 K.

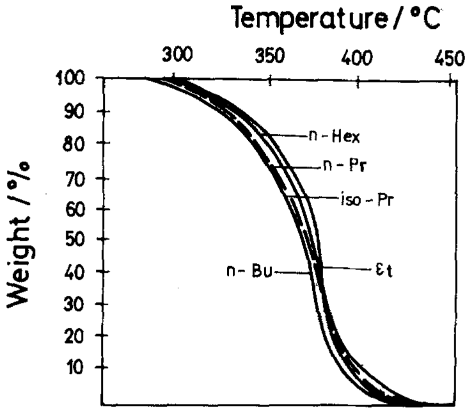

Figure 2. Thermogravimetric analysis of poly(α-MeSt-alt-RMI) in a nitrogen stream; heating rate $10^{\circ}C$/ min.

By applying the semiquantitative treatment described by Shirota and Mikawa (11,12) which is based on the assumption that alternating copolymers are formed by simultaneous cross propagation of free monomers and addition of CT-complex: $R_p = R_p(f) + R_p(CT)$, it was found that in the copolymerization of α-MeSt with EtMI, the reaction proceeds predominantly via the cross propagation of free monomers as shown in Figure 3. The data in Figure 3 and 4 are obtained in the same manner as previously described in the copolymerization of α-MeSt with MeMI (2) and are constructed on the basis of equation 1 (11,12):

$$R_p/[M_1] = A(X).K(k_{1c}/k_{12} + k_{2c}/k_{21}X)[M_1] + A(X) \qquad (1)$$

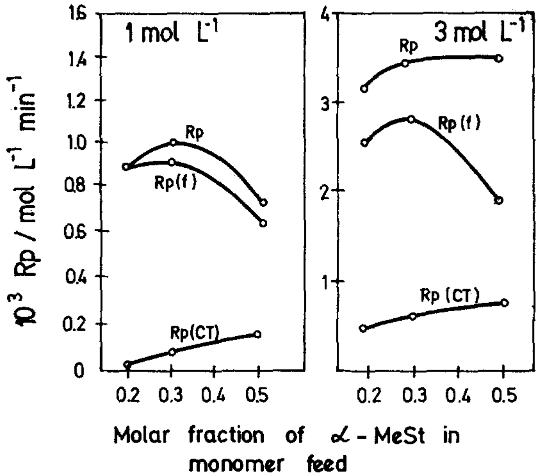

Figure 3. Relative participation of free monomers and CT-complex in the copolymerization of α-MeSt with EtMI at different monomer feed concentrations; $CHCl_3$; $60^{\circ}C$; 0.3 wt/% AIBN

Based on the same procedure, the participation of CT-complex in copolymerization of α-MeSt with iso-PrMI is shown in Figure 4. It is evident that in the presence of bulky substituent, the copolymerization predominantly proceeds via the addition of complex and that by increasing the total monomer concentration the participation of complex increases. This is in agreement with the results previously described for the copolymerization of PhVAE with MAn (13,14).

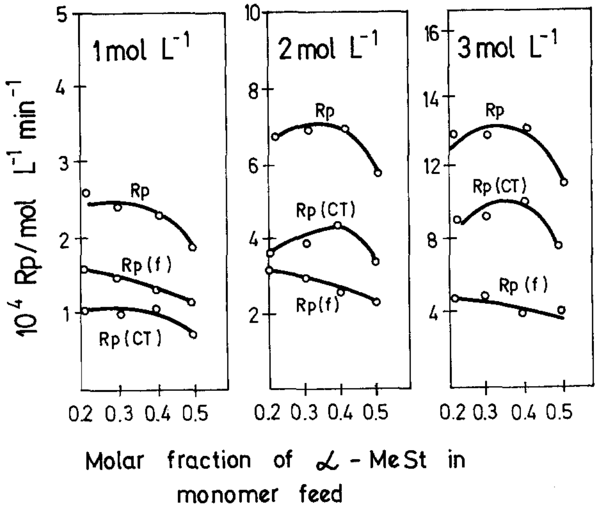

Figure 4. Relative participation of free monomers and CT-complex in the copolymerization of α-MeSt with iso-PrMI at different monomer feed concentrations; $CHCl_3$; 60°C; 0.3/% AIBN.

Following procedure previously described (1,2) the reactivity ratios in the copolymerization of α-MeSt with iso-PrMI are calculated from the slope of straight lines obtained on the basis of eq.1: $Kk_{1c}/k_{12} = 0.4$; $Kk_{2c}/k_{21} = 1.2$; $k_{1c}.k_{21}/k_{2c}.k_{12} = 0.33$. It is evident from these values that the rate of formation of electron donor free radicals ($k_{2c}.k_{12}$) is faster than the rate of formation of electron-acceptor free radicals, thus indicating that the addition of iso-PrMI proceeds predominantly through CT-complex. This conclusion is in agreement with the data obtained in high conversion copolymerization under different monomer-to-monomer ratios in the feed (15,16), as examplified in copolymerization of α-MeSt with iso-PrMI in Figure 5.

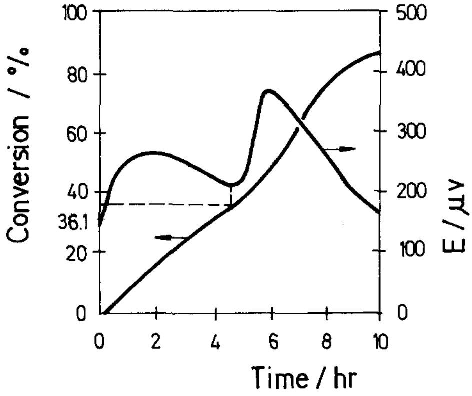

Figure 5. Copolymerization of α-MeSt with iso-PrMI at molar ratio of 0.2 (α-MeSt) to 0.8 (iso-PrMI) in $CHCl_3$ at 60°C with 0.3 wt/% AIBN

In Table 3 are presented nummerical data of theoretical and experimental yields of alternating copolymers of α-MeSt with iso-PrMI.

Table 3. Comparison of theoretical and experimental conversion of alternating copolymers of α-MeSt with RMI at 60°C in $CHCl_3$; 0.3 wt/% AIBN; total monomer concentration 2 mol.L^{-1}.

Molar ratio		Conversion of alt copolymers/%		Molar ratio		Conversion of alt copolymers/%	
α-MeSt	RMI	Theoretical	Experimental	α-MeSt	RMI	Theoretical	Experimental
R = Et				R = n-Pr			
0.1	0.9	19.6	18.2	0.1	0.9	18.8	16.8
0.2	0.8	39.2	38.0	0.2	0.8	38.1	39.2
0.3	0.7	59.3	57.8	0.3	0.7	58.1	60.1
0.4	0.6	79.5	84.5	0.4	0.6	78.7	80.0
R = iso-Pr				R = n-Bu			
0.2	0.8	38.1	36.1	0.2	0.8	37.1	37.7
0.3	0.7	58.1	56.1	0.3	0.7	57.0	60.0
0.4	0.6	78.7	84.0	0.4	0.6	78.0	82.0[a)]
R = n-Hex							
0.2	0.8	35.5	35.0				
0.3	0.7	53.3	61.0[a)]				
0.4	0.6	76.8	84.0[a)]				

[a)] broad minimum in calorigram

Data in Figure 5 and Table 3 indicate that alternating copolymers are formed prior to homopolymerization, and since in all cases homopolymerizable RMI was in excess, it indicates that addition of α-MeSt is preferentially done through CT-complex.

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