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TERPOLYMERS OF MALEIC ANHYDRIDE, 2-ETHYLHEXYL ACRYLATE, AND STYRENE†

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ABSTRACT

Terpolymerization of maleic anhydride, 2-ethylhexyl acrylate, and styrene in homogeneous and heterogeneous conditions was studied. The apparent monomer reactivity ratios were calculated by using the optimization method.

INTRODUCTION

Functional maleic anhydride copolymers and terpolymers offer wide possibilities for modification reactions. The literature of these polymers is very extensive. It is reviewed in Trivedi-Culbertson's [1] and Rzajev's [2] books. However, the terpolymers of maleic anhydride, 2-ethylhexyl acrylate, and styrene have not been described up to now. The physical and physicomechanical properties of these terpolymers are determined by the bulky hydrophobic 2-ethylhexyl acrylate units, which have an internal softening effect.

In this paper the preparation and composition of maleic anhydride–2-ethylhexyl acrylate–styrene terpolymers in homogeneous and heterogeneous conditions is studied. The apparent monomer reactivity ratios are calculated for homogeneous and heterogeneous ternary systems.

†Dedicated to Otto Vogl on the occasion of his 65th birthday.

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EXPERIMENTAL

Materials

Maleic anhydride (MAn) (Lachema, Brno). This commercial reagent was purified by sublimation.

Styrene (ST) (Kaučuk, š. p. Kralupy). This commercial reagent was washed successively with 10% sodium hydroxide and water. The dried styrene was then distilled at reduced pressure under a nitrogen atmosphere.

2-Ethylhexyl acrylate (2EHA) (Chemické závody. Sokolov). This commercial reagent was distilled in vacuum under a nitrogen atmosphere.

Benzoyl peroxide (BP). This commercial reagent was precipitated three times from chloroform solution by methanol and dried in vacuum.

α,α'-Azobisisobutyronitrile (AIBN). This was recrystallized from acetone solution three times, filtered, and dried in vacuum before use.

Solvents and other chemicals used were reagent grade.

Polymerization

Terpolymers were prepared by bulk polymerization and by heterogeneous polymerization in benzene.

1. Homogeneous bulk polymerization was carried out in a sealed tube under a nitrogen atmosphere at 70 ± 0.2°C. The product was precipitated from the reaction mixture by isopropanol, filtered off, dried in vacuum, and analyzed.
2. Heterogeneous polymerization was carried out in a reaction flask equipped with stirrer, cooler, and inlet tube for N_2. The polymerization was run in benzene solvent at 70°C. During polymerization, the terpolymer that formed was precipitated from the benzene solution. At the end of the reaction period, the reaction mixture was cooled, and the product was collected by filtration, washed with benzene, dried in vacuum, and analyzed.

Analysis of Terpolymers

In order to determine the compositions of the MAn, 2EHA and ST terpolymers, gas chromatography was used and the infrared (IR) and nuclear magnetic resonance (NMR) spectra were measured.

After stopping polymerization, gas chromatography of the monomer residue was carried out by means of a CARLO ERBA chromatograph using acetone as the solvent and butyl acetate (BA) as the internal reference at 50 to 170°C (programmed heating); detector, 175°C; injector, 150°C; injection, 10 μL; rate of air–helium mixture flow, 52 cm^3/min.

The contents of unreacted monomers in the reaction mixture (in mass%) were calculated from the peak areas:

$$\text{mass \% of A} = \frac{P_A}{P_s} \cdot \frac{w_m}{w_s} \cdot RF_A \cdot 100$$

where P_A and P_s are the peak areas of Monomer A and the standard (BA), respectively

w_s and w_m are the masses of the standard and analyzed mixtures, respectively

RF_A is the response factor of Monomer A

Response factors of monomers in the mixture were found from calibration of the mixture of monomers and the internal reference (BA). The response factors of styrene and 2-ethylhexyl acrylate are $RF_{ST} = 0.950$ and $RF_{2EHA} = 1.361$.

The ^{13}C-NMR spectra were measured with a JEOL FX-100 spectrometer using deuteroacetone as the solvent at 50°C. Field modulation, 25.047 MHz; induction of magnetic field, 2.3 Tesla; spectral range, 6000 Hz; 5000 accumulations. The chemical shifts of the carbons in the anhydride and ester carbonyl groups (174 and 171.5–173.5 ppm), in the phenyl group (129.25 ppm) and in the $-O-CH_2-$ group of 2EHA (66.94 ppm) were used for evaluation of the molar ratio of monomers in the terpolymers: 2EHA:MAn:ST = A:B/2:C/5, where A, B, and C are the integrated intensities of the signals (A = D).

A Philips model PU 9512 recording infrared spectrophotometer was used to obtain the infrared data. IR spectra were measured by the KBr technique (2 mg sample/1 g KBr). The composition of the terpolymers was determined on the basis of their integrated absorptivities. Details on the use of this method are reported in another paper [3].

RESULTS AND DISCUSSION

Homogeneous bulk terpolymerization of MAn with 2EHA and ST was carried out at a constant equimolar ratio of MAn:ST in the monomer feed at an initiator concentration of [BP] = 4.13×10^{-3} mol/kg and 70°C. The degree of conversion was kept below 20%. As mentioned above, the composition of the terpolymers was determined by gas chromatography at a known conversion and by ^{13}C-NMR spectrometry.

Figure 1 shows the gas chromatogram of a mixture of ST, 2EHA, and BA (molar ratio 1:1:1) in acetone.

The ^{13}C-NMR spectrum of the MAn/2EHA/ST terpolymer is shown in Fig. 2. Table 1 shows the experimental and calculated [with the help of the estimated apparent monomer reactivity ratios (mrr)] composition of the terpolymers.

The apparent mrr's in the ternary system were calculated by an optimization method using Rosenbrock algorithm II [4]. This method is iterative, and the minimum of the objective function (OF) is searched directly. The calculation is carried out by successive approximations from the beginning with an arbitrary starting value to a final one, and fulfills the following condition:

$$|OF^{(k+1)} - OF^{(k)}| = \epsilon$$

where ϵ is the maximal difference of values of the objective function after the $(k + 1)$ and (k) approximations.

The objective function can be represented by

$$OF_i^{(k)} = (LS_i^{(k)} - RS_i^{(k)})$$

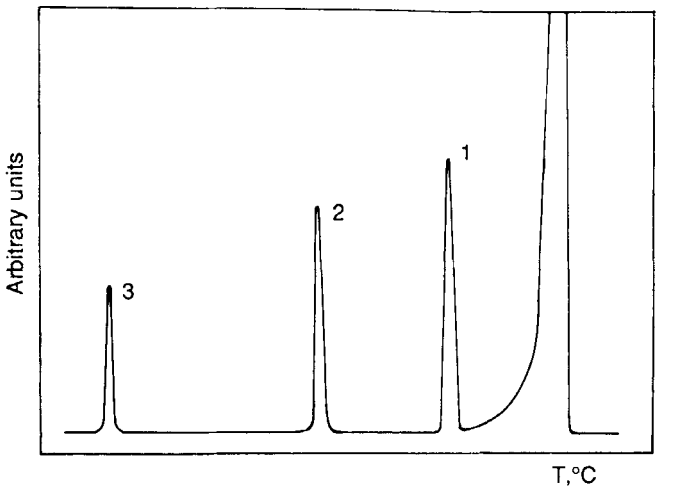

FIG. 1. Gas chromatogram of a mixture of ST, 2EHA, and BA (molar ratio 1:1:1) in acetone. 1: BA (T = 84.5°C); 2: ST (T = 107°C); 3: 2EHA (T = 134°C).

where $LS_i^{(k)}$ and $RS_i^{(k)}$ are the left and right sides of the terpolymerization equation [5] in modified form [6]:

$$F_1 f_2 \cdot \left[\frac{f_1}{r_{12}r_{31}} + \frac{f_2}{r_{12}r_{32}} + \frac{f_3}{r_{32}r_{13}}\right] \cdot \left[f_2 + \frac{f_1}{r_{21}} + \frac{f_3}{r_{23}}\right]$$
$$= F_2 f_1 \cdot \left[\frac{f_1}{r_{31}r_{21}} + \frac{f_2}{r_{21}r_{32}} + \frac{f_3}{r_{31}r_{23}}\right] \cdot \left[f_1 + \frac{f_2}{r_{12}} + \frac{f_3}{r_{13}}\right]$$

where f_i is the mole fraction of the ith monomer in the monomer feed

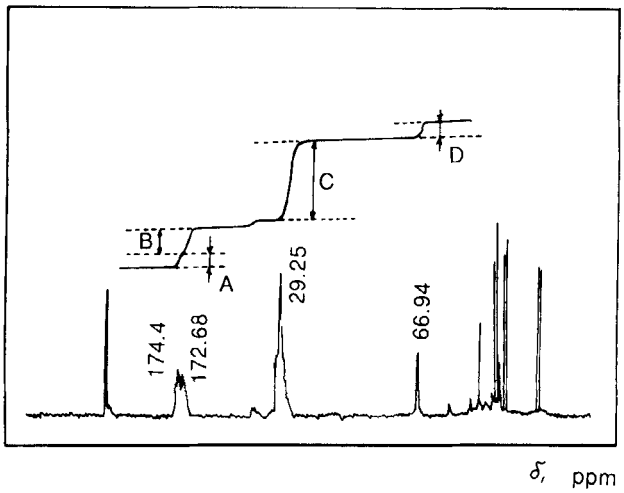

FIG. 2. ^{13}C-NMR spectrum of the MAn/2EHA/ST terpolymer in deuteroacetone at 50°C. Integrated signal intensities of carbons in A: ester carbonyl group; B: anhydride carbonyl group; C: phenyl group (5 carbons); D: $-O-CH_2-$ group 2EHA.

TABLE 1. Homogeneous Terpolymerization of MAn (M_1), 2EHA (M_2), and ST (M_3)

	Monomer feed			Terpolymer composition					
				Experimental value			Calculated value		
No.	f_1	f_2	f_3	F_1	F_2	F_3	F_1	F_2	F_3
I	0.05	0.90	0.05	0.097	0.715	0.185	0.104	0.764	0.132
II	0.10	0.80	0.10	0.258	0.388	0.354	0.275	0.413	0.313
III	0.15	0.70	0.15	0.283	0.354	0.363	0.308	0.385	0.307
IV	0.25	0.50	0.25	0.281	0.380	0.339	0.305	0.412	0.284

TABLE 2. Heterogeneous Terpolymerization of MAn, 2EHA, and ST. Comparison between Experimental mmr of Ternary System and Literature Values of Binary Systems

	Monomer reactivity ratios					
	Experimental values				Arithmetical mean	Literature data [7]
r_{ij}	I	II	III	IV		
r_{12}	0.009	0.054	0.038	0.008	0.027	0.009
r_{21}	3.650	3.902	1.693	2.039	2.821	3.682
r_{13}	0.041	0.037	0.011	0.041	0.033	0.001
r_{31}	0.020	0.019	0.015	0.014	0.017	0.020
r_{23}	0.270	0.259	0.240	0.253	0.256	0.260
r_{32}	0.943	0.912	0.981	0.995	0.958	0.940

TABLE 3. Terpolymerization Rates at Different Temperatures (monomer feed: MAn:2EHA:ST = 1:3:1)

T, °C	55	60	65	70
V_p, %/min	0.90	1.90	3.45	7.46

TABLE 4. Heterogeneous Terpolymerization of MAn, 2EHA, and ST in Benzene at 70°C. Composition of Monomer Feed

Sample	Mole ratio of monomers MAn:2EAH: ST	Weight of components, g				
		MAn	2EAH	ST	Benzene	AIBN
A	1:0.2:1		1.84		130.16	
B	1:0.3:1		2.76		129.24	
C	1:0.4:1	4.9	3.69	5.2	128.31	0.05
D	1:0.5:1		4.61		127.37	
E	1:0.6:1		5.53		126.47	

F_i is the mole fraction of the ith monomer in the terpolymer
r_{ij} $(i \neq j; i, j = 1, 2, 3)$ are monomer reactivity ratios

The mrr of the binary system as obtained from the literature [7] or calculated on the basis of Q-e values (in the case of the MAn/2EHA copolymer) were used as the starting data for the approximation calculation. Table 2 shows the comparison

TABLE 5. Heterogeneous Terpolymerization of MAn, 2EHA, and ST in Benzene (T = 70°C). Terpolymerization Rates and Composition of Terpolymers at Different Monomer Feed Compositions[a]

Sample	Induction period, min	V_p, %/min	Terpolymer composition		
			F_i	Experimental value	Calculated value
A	1.0	0.54	F_1	0.370	0.350
			F_2	0.180	0.170
			F_3	0.450	0.480
B	4.6	0.56	F_1	0.340	0.384
			F_2	0.190	0.214
			F_3	0.470	0.402
C	6.9	0.74	F_1	0.290	0.323
			F_2	0.190	0.212
			F_3	0.520	0.465
D	8.7	0.78	F_1	0.320	0.336
			F_2	0.190	0.199
			F_3	0.490	0.465

[a]Conversions below 16%.

TABLE 6. Heterogeneous Terpolymerization of MAn, 2EHA, and ST in Benzene (T = 70°C). Comparison between Experimental Monomer Reactivity Ratios of Ternary System and Literature Values [7] of Binary System

	Monomer reactivity ratios, experimental values					
r_{ij}	A	B	C	D	Arithmetic mean	Literature data [7]
r_{12}	0.017	0.016	0.015	0.036	0.021	0.009
r_{21}	3.557	2.466	3.570	2.521	3.028	3.682
r_{13}	0.041	0.040	0.039	0.028	0.037	0.001
r_{31}	0.419	0.147	0.399	0.392	0.339	0.020
r_{23}	0.658	0.649	0.221	0.853	0.596	0.260
r_{32}	0.976	1.037	1.242	0.953	1.052	0.940

between the calculated mrr of the ternary (homogeneous) system and those of the binary system.

The effect of temperature on terpolymerization was examined at the molar monomer ratio MAn:2EHA:ST = 1:3:1 in the feed. The initial rate of terpolymerization increases with increasing temperature. Table 3 shows the values of the initial rates at various temperatures. The apparent activation energy calculated from an Arrhenius plot was found to be 129.9 kJ/mol within the 55–70°C temperature range.

Heterogeneous terpolymerization was carried out in benzene solution at an initiator concentration of [BP] = 1.45×10^{-3} mol/kg and [AIBN] = $2,144 \times 10^{-3}$ mol/kg and at 70°C. Table 4 shows the composition of the monomer feeds. The composition of the terpolymers was determined by IR spectrophotometry.

The effects of the composition of the feed on the polymerization rate and on the composition of the terpolymers were examined. The results are summarized in Table 5. It may be seen that the induction period and the initial rate of terpolymerization increase with increasing content of 2EHA in the feed. The correspondence of the experimental and calculated compositions on the basis of the optimization method in the terpolymerization of MAn, 2EHA, and ST is shown in Table 5. Table 6 shows a comparison of the apparent mrr of the ternary system calculated by the optimization method and the mrr of the binary homogeneous system [7].

By comparing the data listed in Tables 3 and 6, the significant differences between the apparent mrr of the heterogeneous ternary system and the mrr of the binary system for the same monomer pairs can be seen.

The mrr's of the monomer pairs MAn–2EHA (r_{12}, r_{21}) and MAn–ST (r_{13}, r_{31}) in the ternary system are dependent on the change of polarity of the system and probably on the change of equilibrium constants of charge-transfer complexes in the presence of the third monomer.

In the case of heterogeneous terpolymerization, it is necessary to assume that all mrr are dependent on differences between the total monomer concentration and the local concentration of monomers around "heterogeneous" propagation centers.

CONCLUSION

The preparation and analysis of MAn/2EHA/ST terpolymers in homogeneous and heterogeneous conditions are described. Apparent monomer reactivity ratios using Rosenbrock's optimization method were calculated. The differences determined between mrr calculated for the ternary system and the literature values of mrr for the binary system can be used as a measure of the influence of the third monomer, solvent, and the heterogeneity of the system on terpolymer compositions.

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