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Macromers

Macromers by Carbocationic Polymerization

6. Copolymerization of α-(p-Vinylphenyl)Polyisobutylene with Methyl Methacrylate and Styrene

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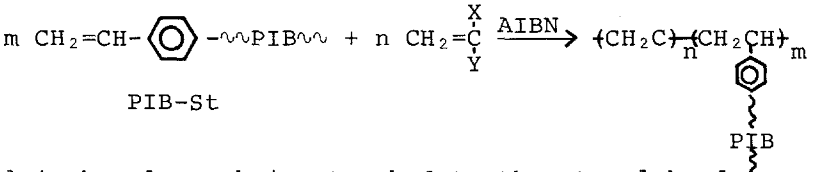
Summary

The reactivity ratio of α-(p-vinylphenyl)polyisobutylene (p-polyisobutenylstyrene, PIB-St) macromers in copolymerization with methyl methacrylate (MMA) and styrene (St) has been examined at various conversions in various solvents and with three macromer chain lengths. Examination of copolymerization reactivity ratios in PIB-St/MMA and PIB-St/St systems indicate that the reactivity of PIB-St with respect to MMA and St comonomers in various solvents is the same as that of styrene. Larger than expected small-comonomer reactivity ratios (r_2) obtained at high conversions and high macromer molecular weights have been attributed to the onset of microphase separation during copolymerization.

Introduction

We have previously described the synthesis and characterization of PIB-St (1). As a continuation of this research it was of interest to examine the free radical copolymerizability of PIB-St with conventional vinyl monomers e.g., MMA, St. The styryl head group (vinylphenyl group) is expected to undergo copolymerization with conventional vinyl monomers and thus graft copolymers can be prepared:



The polyisobutylene chain attached to the styryl head group may affect the reactivity of PIB-St. This paper concerns the preparation of poly(methyl methacrylate-g-isobutylenes) and poly(styrene-g-isobutylenes), and in particular the copolymerization behavior of various molecular weight PIB-St in different solvents and at several conversions. The r_2 value has been determined from the relation $r_2=\ln(1-p_2)/\ln(1-p_1)$ in which p_1 and p_2 are conversions of the macromer and small comonomer, respectively (2).

Materials

The synthesis and purification of PIB-St has been described (1). St and MMA (Aldrich) were washed with 10% aqueous NaOH and water, dried over $MgSO_4$ and freshly distilled. Azobisisobutyronitrile, AIBN, (Eastman) was recrystallized from methanol. Benzene (Fisher), ethyl caproate (Aldrich), ethylbenzene (Aldrich), n-heptane and toluene (Fisher) were freshly distilled.

Polymerization

Copolymerization of PIB-St with St and MMA were carried out in ampules using AIBN initiator in degassed systems (three freeze-and-thaw cycles) at 60°C. Further information is given in the Tables. Polymers were extracted three times with n-pentane to remove unreacted PIB-St. Conversions were determined by ^{1}H-NMR spectroscopy.

Results and Discussions

1. The Effect of Solvent on the Reactivity of PIB-St

In general, the reactivity ratios in free radical copolymerization are rather insensitive to the nature of solvent (3). This generalization, however may not be valid for macromer systems because the conformation of the high molecular weight macromer may be affected by the medium i.e., by polymer-solvent interactions. Thus the accessibility of the reactive site may be different from solvent to solvent.

To investigate the effect of solvent on r_2 copolymerizations of PIB-St/MMA and PIB-St/St have been carried out in n-heptane, ethylbenzene, toluene, and ethyl caproate. The solvent power of these liquids towards PIB follows the sequence: n-heptane > ethylbenzene > toluene > benzene > ethyl caproate (by comparison of respective θ temperatures for PIB).

According to the results with MMA shown in Table I, the r_2 remained the same with 0.55 ± 0.05. This seems to indicate that the reactivity of PIB-St is independent of the solvent, i.e., conformation, during the early stage of the copolymerization with MMA. Further information can be gained by comparing these results with the reported reactivity ratios of conventional $St(M_1)$-$MMA(M_2)$ systems i.e., $r_2=0.5$ (4,5). Evidently, the r_2 values are the same within experimental error. Thus the reactivity of the PIB-St macromer is identical to that of St in copolymerization with MMA.

Similar observations have been made by investigating the copolymerization of PIB-St with St in various solvents. Experimental conditions and results are shown in Table II. The r_2 was 1.0 ± 0.1 in all five cases indicating that the reactivity of the macromer is independent of conformation with St as comonomer. Since r_2 reflects the reactivity ratio of St to that of PIB-St, $r_2=1.0$ indicates that the reactivity of PIB-St and St are identical.

TABLE I

Effect of Solvent on the Copolymerization of PIB-St ($M_n=4.3\text{x}10^3$) [M_1] with MMA [M_2] at 60°C

Solvent	θ Temp.^{a} (°C)	$[M_1]/[M_2]$ in Charge x10^3	$[M_1]/[M_2]$ in Copolymer x10^3	Conv. of M_2 %	r_2 ±0.05
n-Heptane	<-60	4.88	8.48	2.3	0.58
		4.84	2.34	12.2	2.06^b
Ethylbenzene	-24	4.99	9.09	16.2	0.55
Toluene	-13	4.82	10.1	12.3	0.48
Benzene	24	4.86	9.19	16.1	0.52
Ethylcaproate	57	4.80	8.65	15.6	0.55

a. Polymer Handbook, ref. 6
b. Milky solution indicating phase separation

TABLE II

Effect of Solvent on the Copolymerization of PIB-St ($M_n=4.3\text{x}10^3$) [M_1] with St [M_2] at 60°C

Solvent	Temp.^{a} θ (°C)	$[M_1]/M_2]$ in Charge x10^3	$[M_1]/M_2]$ in Copolymer x10^3	Conv. of M_2 %	r_2 ±0.1
n-Heptane	<-60	5.39	5.36	2.5	1.0
Ethylbenzene	-24	5.41	5.02	5.3	1.1
Toluene	-13	5.28	4.98	5.9	1.1
Benzene	24	5.40	5.96	7.2	0.9
Ethylcaproate	57	5.26	5.77	1.1	0.9

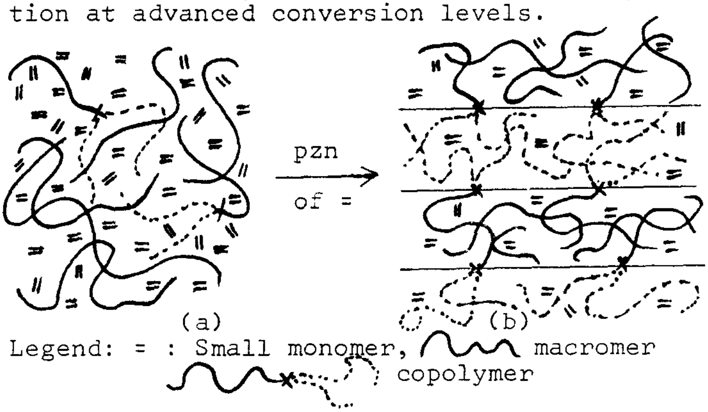
a. Polymer Handbook, ref. 6.

2. The Effect of Conversion on the Reactivity of PIB-St

The effect of conversion on the reactivity of PIB-St has been investigated. Experimental conditions and results are compiled in Table III. It was found that as the copolymerization of PIB-St with St proceeded to higher conversions, the reaction mixtures usually exhibited a bluish tint and the r_2 values became larger than unity. The appearance of the bluish tint is characteristic of microphase separation caused by the incompatibility between the polyisobutylene and polystyrene phases. Figure 1 helps to visualize this phenomenon. At an early stage of the copolymerization, all the components, i.e., PIB-St, St, and a small amount of the graft polymer poly(styrene-*g*-isobutylene), are miscible at the molecular level, and approaches the theoretical value, i.e., 1.0. As the copolymerization proceeds to higher conversions more and more polystyrene units are produced. Due to the incompatibility between polystyrene and polyisobutylene, at a certain

Figure 1

Scheme of phase seperation during the copolymerization of macromer and small monomer in solution. (a) Mixture of macromer, small monomer, and copolymer (b) microphase seperation at advanced conversion levels.



point, microphase separation starts to occur. After microphase separation, the styrene monomer would be partitioned between the two phases so that the observed value of r_2 will be different from that obtained in a homogeneous system. Thus, the deviation of r_2 from the expected (theoretical) value should not be interpreted as a change in macromer reactivity but as an indication of microphase separation in the system.

TABLE III

Dependence of the Reactivity Ratio (r_2) on the Conversion in the Copolymerization[a] of PIB-St (M_1)[b] and St (M_2)

Conv. of St % (p_2)	Conv. of PIB-St % (p_1)	r_2[c]
7.2	7.4	1.0
24.2[d]	21.0	1.2
38.2[d]	29.1	1.4

a. [PIB-St] = 5.2×10^{-3}M, [St] = 0.95M
in benzene at 60°C
b. $\overline{M}_n = 4.2 \times 10^3$
c. $r_2 = \ln(1-p_2)/\ln(1-p_1)$
d. bluish tint indicating phase separation

3. The Effect of PIB-St Molecular Weight on r_2

The preceding discussion concerned the effect of solvents (macromer conformation), and conversion on the reactivity ratio of PIB-St of $\overline{M}_n = 4.9\times10^3$ in copolymerizations with MMA and with St. This section concerns the effect of macromer molecular weight on the reactivity ratio. Three different macromers with $\bar{M}_n$ = 4.8x10^3, 9.6x10^3, and 4.8x10^4 were compared. Two series of copolymerization experiments have been carried out: in the first series the comonomer was MMA, and in the second the comonomer was St. To avoid complications caused by different conversions, only those polymer samples prepared in the vicinity of 20% conversion have been examined. Experimental conditions and results are shown in Tables IV and V.

TABLE IV

Copolymerization of MMA (M_2) with Various Molecular Weights of PIB-St (M_1)^a

$\bar{M}_n$ of PIB-St	Monomer [PIB-St]	Conc. [MMA]	Conv. of PIB-St	Conv. of MMA	PIB^b in Copolymer	r_2
x10^{-3}	x10^{3}M	M	%	%	wt-%	
4.2	6.2	1.0	39.8	22.5	30.7	0.5
9.6	2.7	1.0	41.6	19.3	32.5	0.5
48.0	0.6	1.0	18.7	20.4	20.0	1.1^c

a. with AIBN (0.9 mole-%) as initiator in benzene at 60°C
b. by NMR c. bluish tint indicating phase separation

TABLE V

Copolymerization of St (M_2) with Various Molecular Weights of PIB-St (M_1)^a

$\bar{M}_n$ of PIB-St	Monomer [PIB-St]	Conc. [St]	Conv. of PIB-St	Conv. of St	PIB^b in Copolymer	r_2
x10^{-3}	x10^{3}M	M	%	%	wt-%	
4.2	5.2	0.95	21.0	24.2	16.1	1.2
9.6	2.6	1.0	10.9	21.6	10.7	2.1^c
48.0	0.65	0.94	3.7	22.1	5.0	6.6^c

a. with AIBN (0.9 mole-%) as initiator in benzene at 60°C
b. by NMR c. bluish tint

In the first series of copolymerizations with MMA, r_2 = 0.5 was obtained using macromers of $\bar{M}_n$ = 4.8x10^3 and 9.6x10^3 whereas r_2 = 1.1 was obtained with the macromer of $\bar{M}_n$ = 4.8x10^3. Thus, PIB-St with molecular weights 9.6x10 or lower appear to have the same reactivity as that of styrene (i.e., 0.5±0.1) with MMA as comonomer. The higher r_2 value (i.e., 1.1) obtained with the highest molecular weight PIB-St indicates a lower apparent reactivity of the macromer. The bluish tint that was observed in this copolymerization system indicates microphase separation, which is expected to increase as the molecular weight of the macromer increases.

The results of the second series of copolymerizations with St comonomer are shown in Table V. The same trend was observed, i.e., r_2 increased with the molecular weight of the macromer. The increase of r_2 values relative to the theoretical value of 1.0 was greater than that observed with MMA. Presumably, microphase separation occurs at an earlier stage of the copolymerization in this system.

References

1. Kennedy, J. P. and Lo, C. Y., ACS Polym. Prepr. 23, Number 2, 99 (1982)
2. Kennedy, J. P. and Lo, C. Y., Polym. Bull. 8, 63 (1982)
3. Price, C. C. and Walch, J. G., J. Polym. Sci., 6, 259 (1951)
4. Mayo, F. R. and Lewis, F. M., J. Am. Chem. Soc., 66, 1594 (1944)
5. Kelen, T. and Tüdős, F., J. Macromol. Sci.-Chem., A9(1), 1 (1975)
6. Polymer Handbook, second ed., J. Brandrup and E. H. Immergut, editors, John Wiley Pub., New York, 1975

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