

The Anionic Copolymerization Behavior of the Styrene: p-tert-Butylstyrene and Styrene:p-Methylstyrene Monomer Pairs in Benzene

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Summary

The anionic copolymerization of styrene:p-tert-butylstyrene and styrene:p-methylstyrene has been studied. In benzene, near statistical copolymers can be formed at 20°C when the lithium counter-ion is used. The addition of tetrahydrofuran (THF) is known to disrupt chain end association. The addition of THF (THF/Active center = 10) to the styrene:p-tert-butylstyrene system led to virtually no change in the reactivity ratios.

The copolymerization behavior of relatively few monomer pairs has been investigated in hydrocarbon solvents for systems where organolithiums were used as initiators. Generally, attention has focused on the butadiene:styrene (SPIRIN, et al., 1961; KOROTKOV and CHESHOKOVA, 1961; KUNTZ, 1961; O'DRISCOLL and KUNTZ, 1962; MORTON and ELLS, 1962; JOHNSON and WORSFOLD, 1965; MOCHEL, 1967), isoprene-styrene (ROKOVA and KOROTKOV, 1962; SPIRIN, et al., 1962; WORSFOLD, 1967), and butadiene:isoprene (RAKOVA and KOROTKOV, 1958, 1960; FURUKAWA, et al., 1962; McGRATH and WANG, 1980) pairs. Another monomer pair which has received attention is styrene:p-methylstyrene (O'DRISCOLL and PATSIGA, 1965; O'DRISCOLL, et al., 1965).

Our interest in the copolymerization behavior of styrene and p-tert-butylstyrene was prompted by our intent to use this monomer pair to form terminal copolymer blocks for a thermoplastic elastomer where polybutadiene was the center segment. The morphology, stress-strain behavior and rheological characteristics of this material will be published later. The intent of this note is to present our evaluations of the reactivity ratios for the styrene:p-tert-butylstyrene and styrene:p-methylstyrene pairs.

Experimental Section

The purification of the monomers, benzene and tetrahydrofuran (THF) was done using the procedures described elsewhere (MORTON and FETTERS, 1975). High vacuum techniques were used throughout. Purified, by distillation (BYWATER and WORSFOLD, 1967) sec-butyl-lithium was used as the initiator. This organolithium is known to react rapidly with styrene in benzene. Hence, the copolymer composition was not influenced by a slow initiation reaction. The reaction temperature was 20°C. The degree of conversion was limited to about 5 wt. %. The concentration of initiator was about 10^{-3} M.

The copolymer analysis was carried out on CCl_4 solutions using the Varian 300 MHz $^1\text{H-NMR}$ spectrometer. The method of Fineman and Ross (FINEMAN and ROSS, 1950) was used to determine r_1 and r_2 . The para substituted styrenes were > 95% pure.

Results and Discussion

Table I contains the relevant copolymerization data for the styrene:*p*-tert-butylstyrene and styrene:*p*-methylstyrene monomer pairs.

The data of Table I indicates that near-statistical copolymers will be obtained involving the reported monomer pairs. It should be noted, though, that we have observed that *p*-methylstyrene and its polymer can serve as transfer agents in a manner apparently analogous to toluene (GATZKE, 1969). Hence, it is not possible to prepare high molecular weight linear, near-monodisperse homo- or copolymers using this monomer and the lithium counter-ion at 20°C.

Our results for the reactivity ratios for the styrene:*p*-methylstyrene pair should be compared with the values of $r_1=2.5$ (styrene) and $r_2=0.4$ (O'DRISCOLL and PATSIGA, 1965). Their results were obtained from copolymerization rate studies wherein the disappearance of the two monomers were monitored. It should be noted that the active center concentration used by O'Driscoll and Patsiga was 40 to 50 times larger than that used by us. The influence, if any, of active center concentration on the reactivity ratios of these anionic copolymerization systems is unknown.

Within the limits of experimental error, the relation $r_1 r_2 = 1$ is found to hold for the monomer pairs we examined. In other words:

TABLE I

Copolymer Analysis of Samples Prepared in Benzene

Monomer Pair ^a	[S]	M ₁ /M ₂ ^b	M ₁ /M ₂ ^c
S:t-BS	0.61	1.9 ₆	1.6 ₄
	0.31	0.84	0.76
	0.24	0.45	0.35
	0.74	4.5 ₆	3.1 ₄
	0.79	8.9 ₀	6.8 ₂
$r_1 = 1.34 (+0.12)$ ^d		$r_1 = 0.81 (+0.15)$ ^e	
$r_2 = 0.86 (+0.10)$ ^d		$r_2 = 1.26 (+0.17)$ ^e	
S:p-MS	0.54	2.3 ₉	3.0 ₆
	0.20	0.37	0.44
	0.09	0.14	0.15
	0.33	0.89	1.0 ₈
	0.67	3.8 ₂	4.9 ₉
$r_1 = 0.74 (+0.12)$ ^d		$r_1 = 1.07 (+0.15)$ ^e	
$r_2 = 1.10 (+0.15)$ ^e		$r_2 = 0.70 (+0.09)$ ^e	

^aS = styrene; t-BS = p-tert-butylstyrene; p-MS = p-methylstyrene.

^bM₁/M₂ is the incremental ratio of monomer 1 (Styrene) to monomer 2.

^cM₁/M₂ is the monomer feed ratio where styrene is M₁.

^dCalculated reactivity ratios for the case where styrene is monomer 1.

^eCalculated reactivity ratios where styrene is monomer 2.

$$k_{S-S}/k_{S-MS} = r_1 = k_{MS-S}/k_{MS-MS} = 1/r_2$$

which is in agreement with a kinetic case (YAMAGISHI and SZWARC, 1978) advanced for the styrene:*p*-methylstyrene system wherein it was assumed that the associated chain ends are unreactive.

It is generally agreed that polystyryllithium is associated as a dimer in hydrocarbon solvents. Thus, copolymerizations involving, for example, the monomer pairs described herein would consist of the two self-associated dimers and the cross-associated dimer. If the assumption that only unassociated chain-ends are reactive, the copolymer composition is dependent not only upon the values of the four rate constants but also upon the concentration of the unassociated species; the latter being governed by the respective values of the equilibrium constants of the three associated \rightleftharpoons unassociated equilibria. Hence, the elimination of the associated species could lead to alterations in r_1 and r_2 .

Concentrated solution viscosity measurements (MORTON, et al., 1970) have shown that THF will disrupt polystyryllithium association. This analysis revealed that at an active center concentration of ca. 10^{-3} M, and ether/SLi ratio of 10 will lead to the virtual elimination of the self- and cross-associated dimers. Thus, the evaluation of r_1 and r_2 for the styrene:*p*-tert-butylstyrene system was undertaken with THF present. These results are shown in Table II. A similar study using *p*-methylstyrene was not undertaken in view of the potential complicating feature of enhanced chain transfer caused by the presence of THF.

It can be seen that, within experimental error the reactivity ratios of the THF modified system are identical to those found in pure benzene. Thus, for this monomer pair, the elimination of the associated species by the addition of THF does not alter the respective reactivity ratios. In a circumstantial fashion, these results indicate that the associated chain-ends may be reactive entities of these copolymerizations.

We wish to note that the concept that associated organolithium species are unreactive is based solely on kinetic evaluations and considerations. We are unaware of any obvious or simple reasons as to why the electron deficient bonding present in these associated structures should preclude reactivity of these species.

TABLE II

Copolymer Analysis of Samples Prepared in Benzene/THF Mixtures

$[S]^b$	m_1/m_2	M_1/M_2
0.33	1.0 ₉	0.96
0.52	5.3 ₂	2.9 ₇
0.22	2.1 ₇	2.1 ₉
0.61	10.4	7.3 ₆
0.61	14.7	10.4
0.55	10.2	7.5 ₂
$r_1 = 1.44 (\pm 0.16)^c$	$r_1 = 1.03 (\pm 0.21)^d$	
$r_2 = 1.01 (\pm 0.20)^c$	$r_2 = 1.46 (\pm 0.15)^d$	

a THF/Active centers = 10

b Styrene is monomer 1

c Computed where styrene is monomer 1

d Computed where p-tert-butylstyrene is monomer 1

Brown (BROWN, 1966) noted some years ago that associated organolithiums can be reactive entities.

In conclusion, we wish to mention that p-methylstyrene, unlike p-tert-butylstyrene, is a slightly more reactive monomer than styrene in these copolymerizations (Table I). Consideration of the inductive influence of the methyl group predicts the opposite effect. If the assumption that $k_{MS-MS} < k_{S-S}$, then our results show that $k_{S-MS} > k_{MS-S}$: (where, as before the k 's denote the apparent rate constants for the respective homo- and cross-propagation events). A similar reversal of reactivities has been seen for the styrene:diene monomer pairs, i.e. $k_{S-D} > k_{D-S}$. However, we have no mechanistic explanation to offer for the apparent reversal of reactivities of styrene and p-methylstyrene.

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