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The influence of total monomer concentration on the "reactivity" of ω-(p-vinylbenzyl ether) macromonomers of poly(2,6-dimethyl-1,4-phenylene oxide) determined from radical copolymerization experiments with butyl methacrylate

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SUMMARY

The influence of the total monomer concentration on the radical reactivity ratio r_1 of butyl methacrylate (BMA) (M_1)-ω-(p-vinylbenzyl ether) macromonomer of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-VBE) (M_2) monomer pair was investigated. For two different molecular weights of the PPO-VBE macromonomer ($\overline{M}_n$=14,000, $\overline{M}_w/\overline{M}_n$=1.25 and $\overline{M}_n$=5,300 $\overline{M}_w/\overline{M}_n$=1.26), the determined reactivity ratio r_1 decreases with the increase of the macromonomer concentration. Therefore, the reactivity of the macromonomer, $1/r_1$, follows the opposite trend. This dependence is due to micelles formation during copolymerization. This microsegregation process partitionates the comonomer concentrations between the bulk of solvent and around the growing chain and therefore, the experimental r_1 is actually a product of the true reactivity ratio r_1^o and a partition coefficient k.

INTRODUCTION

The radical reactivity ratios of many pairs of polar monomers have been reported to depend on the nature and the concentration of the solvent used in copolymerization (1). Harwood et al. (2) have reinvestigated some of these copolymerization systems and demonstrated that the sequence distribution of the copolymers of identical composition but synthesized in different solvents is the same. Therefore, these copolymers are obtained by a similar copolymerization mechanism and the difference between the values of reactivity ratios obtained in different solvents are due to experimental artifacts. He proposed the "bootstrap model" to account for the monomer concentration difference around the growing chain and the bulk of the free solvent, which is responsible for the different reactivity ratios obtained in different solvents.

The copolymerization of a macromonomer-low molecular weight monomer pair resembles the copolymerization of polar monomer pairs since the solubility of the macromonomer is both molecular weight and concentration dependent. Although the reactivity of macromonomers should be molecular weight independent, several research groups have reported that their reactivity is molecular weight (3-13) or even conversion dependent (10). This dependence has been attributed to the kinetic excluded volume effects (3, 11), thermodynamic repulsive interactions (11, 13) and the onset of microphase separation of the reaction mixture (10, 14, 15).

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Previous results (14) from our laboratory have demonstrated that the reactivity of ω-(p-vinylbenzyl ether) macromonomer of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-VBE) determined from radical copolymerization experiments with methyl methacrylate (MMA) increases with total monomer concentration. The nature of the polymerization solvent was found also to affect the reactivity of the macromonomer. These results were explained based on the microphase separation of the reaction mixture, i.e. micelles formation during the copolymerization process.

The goal of this paper is to describe the influence of the total monomer concentration on the reactivity of PPO-VBE macromonomer with two dissimilar molecular weights. The reactivity ratio of butyl methacrylate (BMA, r_1) of which reciprocal ($1/r_1$) represents the reactivity of PPO-VBE, was determined from radical copolymerization experiments using BMA as comonomer.

EXPERIMENTAL

The experimental details concerning the synthesis of the macromonomer (3,16), the radical copolymerization experiments and the kinetic experiments used to determine r_1 values (3,14) have been described previously. Two PPO-VBE macromonomers with $\bar{M}_n$=5,300; $\bar{M}_w/\bar{M}_n$=1.26 and $\bar{M}_n$=14,000; $\bar{M}_w/\bar{M}_n$=1.25 were used. The copolymerization experiments were performed in toluene at 60°C and with α,α'-azobisisobutyronitrile (AIBN) as radical initiator.

RESULTS AND DISCUSSION

For the comonomer pair butyl methacrylate (M_1)-PPO-VBE (M_2), the reactivity ratio, r_1, was determined as the slope of the $-\log[M_1]_t/[M_1]_o$ versus $-\log[M_2]_t/[M_2]_o$ plot (3,14). The experimental conditions and the results obtained from the copolymerization of PPO-VBE (M_2) ($\bar{M}_n$=14,000 and $\bar{M}_w/\bar{M}_n$=1.25) with BMA at several different total monomer concentrations are listed in Table I. $[M_1]/[M_2]$ was maintained constant so that the total monomer concentration is proportional to $[M_2]$. The sequence length of BMA structural units in the resulting graft copolymer, assuming only one PPO graft per graft copolymer, n_1', was calculated based on the $\bar{M}_n$ of the resulting graft copolymer determined from GPC measurements. Except for the experiment performed at the highest $[M_2]$ (experiment 6 in Table I) all other graft copolymers have incorporated shorter BMA sequences than the expected theoretical n_1, i.e. $n_1'<n_1$. This implies that the values of r_1 are not representative since the resulting graft copolymer contains on average less than one PPO graft. A correction was made to compare the corresponding r_1' (obtained from n_1' and $[M_1]/[M_2]$) with the r_1' of the copolymer with the highest n_1'. The converted r_1' (corrected) values are given in the last column in Table I. The variation of r_1 as a function of $[M_2]$ is plotted in Figure 1. Curve A represents the experimental r_1 for $\bar{M}_n$=14,000 while the corrected r_1 is plotted as curve B. These results have shown that both r_1 and n_1 decrease with the increase in $[M_2]$.

For the copolymerization of PPO-VBE ($\bar{M}_n$=5,300 and $\bar{M}_w/\bar{M}_n$=1.26) with BMA, the corresponding results are summarized

Table I. The Influence of Macromonomer Concentration on the r_1 Determined from the Radical Copolymerization of BMA (M_1) with PPO-VBE (M_2, $\overline{M}_n$=14,000; $\overline{M}_w/\overline{M}_n$=1.25); Polymerization Solvent, Toluene; Polymerization Temperature, 60°C; Initiator, AIBN.

Exp. No.	M_1 (g)	M_2 (g)	AIBN (mg)	Toluene (g)	$[M_1]/[M_2]$ mol/mol	$[M_2]$ ($X10^{-3}$mol/l)	r_1	n_1 $(r_1\frac{[M_1]}{[M_2]}+1)$	$\overline{M}_n$ (g/mol) of Graft Copolymer (by GPC)	Calculated $\overline{M}_n$ of Graft Copolymer Repeat Unit (g/mol) $(\overline{M}_n(2)+M_1 \times n_1)^a$	$n_1{}'^{,b}$	$r_1{}'^{,c}$	$\frac{n_1'}{n_1}$ X100	$r_1{}'^{,d}$ (corrected)
1	2.0021	0.3946	50.0	12.1327	500	2.01	0.90	451	38,900	78,000	175	0.348	39	0.81
2	2.0124	0.3946	50.0	6.9320	500	3.52	0.90	451	41,500	78,000	194	0.386	43	0.82
3	2.0100	0.3946	50.0	5.2080	500	4.69	0.83	416	61,500	73,100	335	0.688	81	0.75
4	2.0036	0.3946	39.0	4.1685	500	5.86	0.83	416	57,600	73,100	307	0.612	74	0.75
5	2.0003	0.3946	32.0	3.4577	500	7.03	0.84	421	68,700	73,800	385	0.768	91	0.77
6	2.0125	0.3946	20.0	2.6005	500	9.38	0.74	371	137,700	66,700	871	1.740	235	0.74

a) M_1 = Molecular weight of BMA; $\overline{M}_n(2) = \overline{M}_n$ of M_2.

b) $n_1' = \frac{\overline{M}_n \text{ (Graft Copolymer)} - \overline{M}_n(2)}{M_1}$, i.e., it is assumed that the graft copolymer contains only one repeat unit.

c) $r_1' = (n_1'-1)/([M_1]/[M_2])$.

d) r_1' (corrected) $= r_1' \times \frac{n_1' \text{ (exp. No. 5)}}{n_1'}$, i.e., r_1' is compared to the r_1' with the highest n_1'.

Table II. The Influence of Macromonomer Concentration on the r_1 Determined from the Radical Copolymerization of BMA (M_1) with PPO-VBE (M_2, $\overline{M}_n$=5,300; $\overline{M}_w/\overline{M}_n$=1.26); Polymerization Solvent, Toluene; Polymerization Temperature, 60°C; Initiator, AIBN.

Exp. No.	M_1 (g)	M_2 (g)	AIBN (mg)	Toluene (g)	$[M_1]/[M_2]$ mol/mol	$[M_2]$ ($\times 10^{-3}$ mol/l)	r_1	n_1 $(r_1\frac{[M_1]}{[M_2]}+1)$	$\overline{M}_n$ (g/mol) of Graft Copolymer (by GPC)	Calculated $\overline{M}_n$ of Graft Copolymer Repeat Unit (g/mol) $(\overline{M}_n(2)+M_1 \times n_1)^a$	$n_1'^{\,b}$	$r_1'^{\,c}$	$\frac{n_1'}{n_1} \times 100$
1	2.0015	0.1445	10.7	12.1240	500	2.01	0.71	356	88,000	55,900	582	1.162	163
2	1.9999	0.1445	10.7	6.9280	500	3.52	0.70	351	125,500	55,100	846	1.690	241
3	2.0003	0.1445	16.1	5.1960	500	4.69	0.64	321	120,900	50,900	815	1.628	254
4	2.0021	0.1445	10.7	4.1569	500	5.86	0.64	321	159,300	50,900	1085	2.168	338
5	2.0040	0.1445	10.7	3.4691	500	7.03	0.63	316	198,300	50,200	1359	2.716	430
6	2.0021	0.1445	8.0	2.6000	500	9.38	0.64	321	230,400	50,900	1585	3.168	494

a) M_1 and $\overline{M}_n(2)$ are the molecular weights of BMA and number average molecular weight of M_2, i.e., macromonomer, respectively.

b) $n_1' = \frac{\overline{M}_n\text{ (Graft Copolymer)} - \overline{M}_n(2)}{M_1}$, i.e., it is assumed that the graft copolymer contains only one repeat unit.

c) $r_1' = (n_1'-1)/([M_1]/[M_2])$; r_1' is not meaningful here since in most cases $n_1' > n_1$.

in Table II. In this case, the calculated n_1' values are larger than the theoretical n_1, i.e. the graft copolymers have higher molecular weights than expected for a copolymer with only one PPO graft per molecule. Therefore, for these series of experiments the r_1'values are not meaningful. However, the experimental r_1 values are reliable. These data were plotted as curve C in Figure 1. The r_1 values and n_1 also decrease with the increase in $[M_2]$.

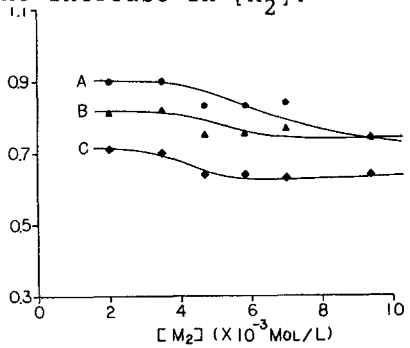

Figure 1. The dependence of r_1 on the concentration of PPO-VBE macromonomer $[M_2]$ in the monomer feed: A) $\overline{M}_n$ = 14,000; $\overline{M}_w/\overline{M}_n$ = 1.25, experimental data; B) $\overline{M}_n$ = 14,000; $\overline{M}_w/\overline{M}_n$ = 1.25, corrected data, r_1' (corrected); C) $\overline{M}_n$ = 5,300; $\overline{M}_w/\overline{M}_n$ = 1.26, experimental data.

During the copolymerization process the reaction mixtures containing the low molecular weight PPO-VBE macromonomer remain clear. However, the reaction mixtures containing the high molecular weight PPO-VBE become turbid towards the end of copolymerization.

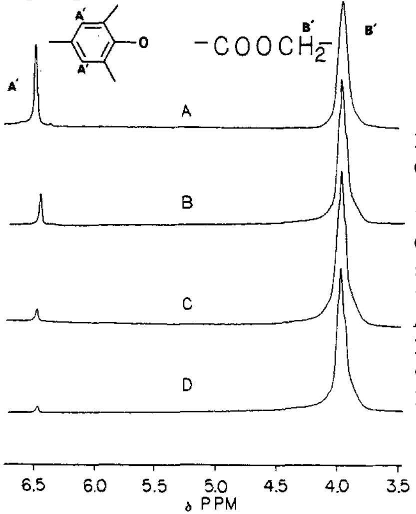

Figure 2. 200 MHz ^{1}H-NMR spectra of PBMA-g-PPO graft copolymer (polymer from experiment 4 in Table I) in different ratios of $CDCl_3$ to CD_3COCD_3 (v/v), (TMS as internal standard), 55°C; expansion of 3.5 to 6.7 ppm region of the spectra:
A) $CDCl_3/CD_3COCD_3$ = 1/0
B) $CDCl_3/CD_3COCD_3$ = 1/1
C) $CDCl_3/CD_3COCD_3$ = 1/3
D) $CDCl_3/CD_3COCD_3$ = 1/5.

200 MHz ^{1}H-NMR experiments were performed on the graft copolymer no. 4 in Table I in different mixtures of $CDCl_3$ and CD_3COCD_3 to estimate the homogeneity of the reaction mixture. This mixture of solvents resembles the solubility behavior of BMA-toluene which represents the real polymerization solvent. These experiments demonstrate that the graft copolymer forms micelles even when the polymerization mixture is transparent and resembles an ideal solution (Figure 2). Acetone is a good solvent for PBMA only. As the volume of acetone in the solvent mixture increases, the integral of the aromatic region derived from PPO grafts decreases. The quantitative data of the

integrals are shown in Figure 3. This phenomenon can be easily understood in terms of micelles formation as outlined in Figure 4.

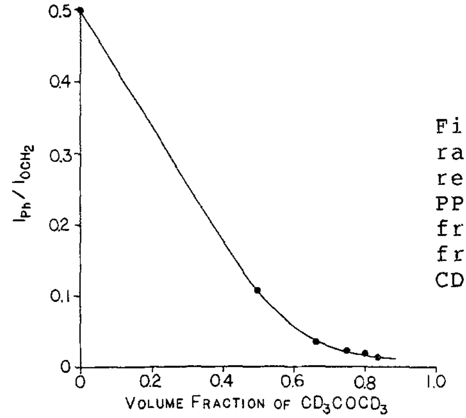

Figure 3. The dependence of the ratio of the integrals of proton resonances for phenylene units of PPO (I_{ph}) to methyleneoxy groups from PBMA (I_{OCH2}) on the volume fraction of CD_3COCD_3 in the $CDCl_3/CD_3COCD_3$ solvent mixtures.

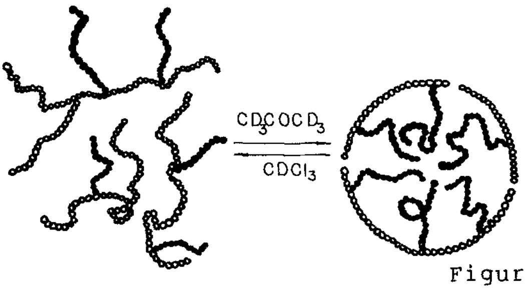

Figure 4: Schematic representation of micellar structure of PBMA-g-PPO in mixtures of $CDCl_3/CD_3COCD_3$ solvents.

The dependence of r_1 versus $[M_2]$ can be explained in terms of micelles formation during the copolymerization process. A schematic picture of the copolymerization system is presented in Figure 5. Since the solubility of PPO-VBE (M_2) macromonomer in toluene is higher than that of PBMA, the PPO grafts are oriented to point to the toluene rich direction (i.e. outside

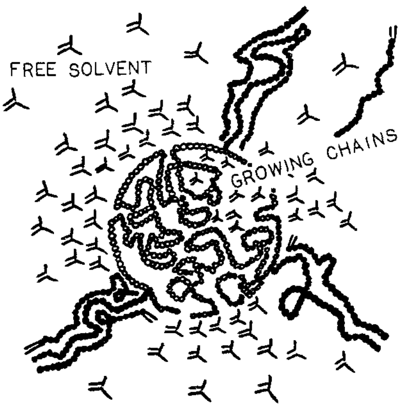

Figure 5. Schematic representation of macromonomer concentration partition between growing chain and bulk of free solvent during polymerization.

of the micelle). A concentration partition of PPO-VBE and BMA similar to that proposed by Harwood (2) for the case of pairs of polar monomers, can be considered for this copolymerization system. The experimentally determined r_1' data are actually a product of r_1^o (true reactivity ratio as defined in the terminal model of copolymerization) and a partition coefficient k (14).

$$r_1 = r_1^o * k \qquad (1)$$

$$k = \frac{[M_1]_{chain}/[M_1]_{bulk}}{[M_2]_{chain}/[M_2]_{bulk}} \qquad (2)$$

The concentration of micelles in this reaction mixture is determined by the total monomer concentration and the extent of the copolymerization reaction, which changes continuously both the concentration of graft copolymer and the composition of the copolymerization solvent. Therefore, as $[M_2]$ or the total monomer concentration increases, the concentration of micelles and accordingly the extent of partition increases, i.e. $[M_2]_{chain}/[M_2]_{bulk}$ increases with $[M_2]$. This causes the determined r_1 to decrease with the increase in $[M_2]$.

As shown in Figure 1, for the same $[M_2]$ the r_1 value of PPO-VBE with $\bar{M}_n$=14,000 is higher than that of PPO-VBE with $\bar{M}_n$=5,300. The increase of r_1 with the increase of the macromonomer molecular weight has been previously observed for this PPO-VBE (3). Based on the micelles formation model, one would expect the extent of micelles formation to be higher for higher molecular weight macromonomers, and therefore higher molecular weights macromonomers would accordingly give lower r_1 values for the same overall monomer concentration. However, the micelles formation and the partition of macromonomer concentration requires also the reasonable transportation of unpolymerized macromonomer molecules from solution into micelle to be considered. As the molecular weight of the macromonomer increases, its coil size increases and therefore, the diffusion of the macromonomer molecules from bulk of solution in and out of the micelles becomes slower (Figure 5). This effect may decrease the concentration of the macromonomer within the micelle, and eventually could provide r_1 values which are higher than those obtained for a lower molecular weight macromonomer. The experimentally determined r_1 values reflect the net effect of both factors. However, the experimental results have indicated the kinetic transportation as being the predominate factor.

CONCLUSIONS

For BMA (M_1) -PPO-VBE (M_2), the determined reactivity ratio r_1 decreases with the increase of total monomer concentration. The reactivity of PPO-VBE (M_2) macromonomer, $1/r_1$, increases with the total monomer concentration. This trend was observed for PPO-VBE macromonomers with two different molecular weights. Micelles formation was demonstrated by ^{1}H-NMR spectroscopy performed on the resulting graft copolymer in different solvent mixtures. Therefore, the dependence of r_1 on the total monomer concentration seems to be the result of the nonideality of the polymerization mixture.

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