

Copolymerization

Poly(Ethylene Oxide) Macromonomers 3.* Solvent Effects on the Macromonomer's Reactivity in Radical Copolymerization

Koichi Ito, Hiroyuki Tsuchida, and Toshiaki Kitano**

School of Materials Science, Toyohashi University of Technology,
Tempaku-cho, Toyohashi 440, Japan

Summary

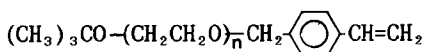
p-Vinylbenzyl-terminated poly(ethylene oxide) macromonomers (M_2) were radical-copolymerized with styrene (M_1) in benzene, tetrahydrofuran, and methyl isobutyl ketone at 60°C. Relative reactivity of the macromonomer toward polystyryl radical, as estimated by $1/r_1$, was found to decrease with increasing number-average degree of polymerization and also in a solvent which gives a higher $[\eta]$ of both polystyrene and the macromonomer. The results support our previous suggestion that a repulsion between the macromonomer and the propagating polymer radical can be a factor responsible for disturbing their mutual reaction.

Introduction

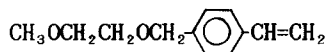
Macromonomer method is now a well-known approach to graft copolymers via simple copolymerizations of a branch-forming macromonomer and a variety of trunk-forming comonomers. However, only limited data are available on the relevant monomer reactivity ratios which are very important in determining the trunk-branch ratio and distribution in the resulting graft copolymers. In our previous paper (1), poly(ethylene oxide) macromonomers carrying p-vinylbenzyl (PEO-VB) and methacrylate (PEO-MA) as the end-groups were radical-copolymerized with styrene (M_1) in tetrahydrofuran (THF) at 60°C, with the result that the macromonomer's relative reactivity ($1/r_1$) decreased by a factor as much as about 1/2 with increasing degree of polymerization. We proposed a generally repulsive interaction between different polymer chains, a macromonomer and a propagating polymer radical in this case, as a factor responsible for the reduced macromonomer's reactivity. In support of this proposal, we describe in the present paper the solvent effect in radical copolymerization of PEO-VB with styrene. 2-Methoxyethyl p-vinylbenzyl ether (MEO-VB) is used as a model monomer of low molecular weight.

* Part 1: Ref. 1, Part 2: Ref. 2

**Present address: Tsukuba Research Lab., Hitachi Maxell Co., Ltd., 6139-1, Oonogou-machi, Mitsukaido, Ibaragi 300-25, Japan



PEO-VB



MEO-VB

Results and Discussion

Table 1 shows the result of characterization of the macromonomers PEO-VB-*n*, newly prepared after the previous paper (1), *n* standing for the number-average degree of polymerization of ethylene oxide determined by VPO. Other methods including ¹H NMR, UV, and GPC gave almost the same *n* values, justifying their satisfactory purity. The molecular weight distribution was also sharp enough as estimated by GPC.

Copolymerizations were conducted at 60°C with α, α'-azobisisobutyronitrile (AIBN) as the initiator in THF, benzene, and methyl isobutyl ketone (MIBK) as the solvents. Benzene and MIBK were chosen as the good and poor solvents, respectively, for both poly(ethylene oxide) and polystyrene. MIBK is a theta solvent for poly(ethylene oxide) at 50°C (3). In Table 2, the intrinsic viscosities [η] show the relative degree of expansion of both PEO-VB and polystyrene to decrease in the order of the solvents; benzene > THF > MIBK.

Table 1. Characterization of PEO-VB Macromonomers

Macromonomer code	VPO	NMR ¹	UV ²	GPC ³	
	<i>n</i>	<i>n</i>	<i>n</i>	<i>n</i>	Mw/Mn
PEO-VB-23	22.7	18.7	24.3	23.9	1.07
PEO-VB-57	56.8	47.1	66.6	53.4	1.05
PEO-VB-93	93.2	79.9	98.6	86.6	1.04

¹ Calculated from the ratio of the peak areas of oxyethylene to tert-butyl protons.

² Calculated by using $\epsilon_{\text{max}} = 1.59 \times 10^4$ at $\lambda_{\text{max}} = 252$ nm in THF (4).

³ Using a calibration by PEO standard samples.

Table 2. Intrinsic Viscosities of the Macromonomer (PEO-VB-93) and Polystyrene (Mn 14700) at 25°C

Solvent	[η] /dl g ⁻¹	
	PEO-VB-93	Polystyrene
Benzene	0.111	0.139
THF	0.103	0.131
MIBK	0.080 ¹	0.102

¹ Measured at 49°C.

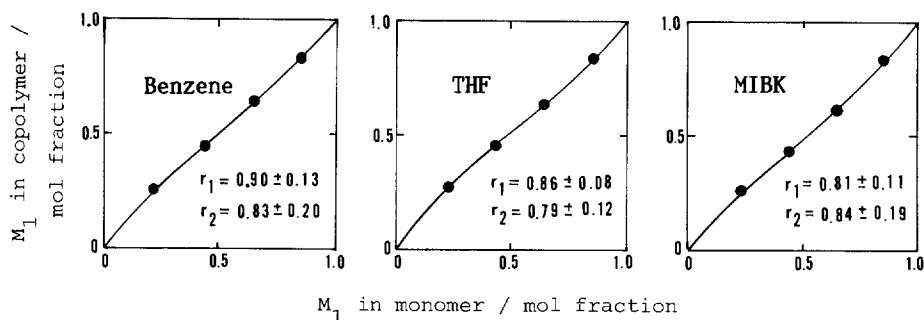


Figure 1. Composition curves for copolymerization of styrene (M_1) with MEO-VB (M_2). Total monomer conc. 10 % w/v, AIBN 1 mol %, 16 h, 17-24 % conv. The monomer reactivity ratios r_1 and r_2 indicated were calculated by Kelen-Tüdös method (5) with the errors of 95 % confidence limit.

Figure 1 shows the results of copolymerization of styrene (M_1) and the model monomer MEO-VB (M_2). As expected, the monomer reactivities were found to depend very little on the polymerization solvent.

The macromonomer's reactivity was estimated as before (1) by copolymerization with a very large molar excess of styrene (M_1), i. e., under the condition of $[M_1] \gg [M_2]$, for the approximate composition equation, $d[M_1]/d[M_2] = r_1[M_1]/[M_2]$, to hold, where $r_1 = k_{11}/k_{12}$. The polymer products isolated and purified were confirmed by GPC to be free of the unreacted macromonomers, and analyzed for the composition by ^1H NMR using the relative peak areas due to the phenyl and the oxyethylene protons. The raw data, given in Table 3, show that the consistent r_1 values were obtained independently of the composition $[M_1]/[M_2]$ over about 70. Their reciprocals, $1/r_1 = k_{12}/k_{11}$, can approximate a simple measure of the relative reactivity of the macromonomer (M_2) toward polystyryl radicals ($\text{--[}M_1\text{]}_n\cdot$, with $n \gg 1$), since a very large molar excess of M_1 is used as the common comonomer throughout the present system and the rate constant k_{11} will hardly change depending on the solvent as compared to k_{12} .

Table 4 summarizes the obtained monomer reactivity ratios (r_1) together with those reported before (1). The data clearly show that the macromonomer's relative reactivity ($1/r_1$) is significantly lower than that of the model monomer and decreases slightly with increasing degree of polymerization. Also the solvent in which both the macromonomer and polystyrene are more expanded apparently lowers the relative reactivity of the macromonomer with n higher than about 50. As expected, polystyrene ($M_n 3 \times 10^4$) and poly(ethylene oxide) ($M_n 1180$) were confirmed to be incompatible to give an unclear or phase-separated film at the ambient temperature from 30 to 170°C.

Table 3. Copolymerization of Styrene (M_1) and PEO-VB (M_2)
 in Benzene and MIBK¹

M_2 n (VPO)	Solvent	$\frac{[M_1]}{[M_2]}$ mol/mol	Polymn. time h	Polym. yield ² wt%	$\frac{d[M_1]}{d[M_2]}$ mol/mol	r_1	r_1 (av) ± 95% conf. limit
23	Benzene	216	20	26.0	360	1.67	1.66 ± 0.03
		144	20	25.1	239	1.66	
		104	20	25.1	170	1.63	
		80	20	24.8	137	1.70	
		72	20	23.7	120	1.66	
57	Benzene	483	20	25.5	869	1.80	1.83 ± 0.04
		316	20	26.2	577	1.83	
		232	20	24.0	432	1.86	
		180	20	4.7	335	1.86	
		147	20	3.7	261	1.78	
93	Benzene	1600	20	28.6	2690	1.68	1.86 ± 0.26
		775	20	25.4	1390	1.79	
		371	20	1.3	699	1.88	
		276	20	0.5	570	2.07	
23	MIBK	217	16	19.2	295	1.36	1.42 ± 0.05
		143	16	18.7	206	1.44	
		102	16	18.1	146	1.43	
		80	16	17.3	118	1.47	
		64	16	17.1	91	1.41	
57	MIBK	483	16	20.7	640	1.33	1.45 ± 0.10
		321	16	19.7	450	1.40	
		230	16	18.7	336	1.46	
		180	16	18.7	268	1.49	
		146	16	17.3	226	1.55	
93	MIBK	1570	16	19.3	2110	1.34	1.46 ± 0.09
		774	16	18.2	1160	1.50	
		499	16	18.4	763	1.53	
		370	16	16.9	545	1.47	
		288	16	12.6	425	1.48	

¹ Total monomer 2 g, Solvent 20 ml, AIBN 1 mol %, 60°C.

² Products isolated by precipitation into methanol. They had M_n of an order of $1.5 \sim 2.0 \times 10^4$ by GPC (calibrated by std. PEO).

Table 4. Monomer Reactivity Ratios of Styrene (M_1) in Copolymerization with MEO-VB and PEO-VB (M_2) in Various Solvents at 60°C

M_2	r_1 in		
	Benzene	THF	MIBK
MEO-VB	0.90 ± 0.13	0.86 ± 0.08	0.81 ± 0.11
PEO-VB-23	1.66 ± 0.03	—	1.42 ± 0.05
PEO-VB-29	—	1.33 ± 0.07 ¹	—
PEO-VB-51	—	1.71 ± 0.05 ¹	—
PEO-VB-57	1.83 ± 0.04	—	1.45 ± 0.10
PEO-VB-93	1.86 ± 0.26	—	1.46 ± 0.09
PEO-VB-94	—	1.79 ± 0.12 ¹	—

¹ Previous data (1).

These results clearly support our previous suggestion (1) that a repulsion between different polymer chains, polystyryl radical and poly(ethylene oxide) macromonomer in the present case, is a factor responsible for reducing their reaction rates. It is important to note that a significant rate reduction occurred even in a poorest solvent, MIBK, which gave the most contracted chains of polystyrene and the macromonomer. It is reasonable to consider that any interaction between different polymer chains will remain to operate even under the condition (θ) which will eliminate the interaction (both intramolecular and intermolecular) between the polymer chains of the same kind.

A recent review (6) appears to reveal a similar tendency in the available data of macromonomers' reactivities as compared to the model monomers. Among these, the methacrylate-terminated poly(dimethylsiloxane) by Cameron and Chisholm (7) and p-vinylbenzyl-terminated polyisobutylene by Kennedy and Lo (8) were found to decrease their reactivities with increasing molecular weights in copolymerization with styrene or methyl methacrylate. The phase-separation was indeed observed during polymerization in the latter case (8). Very recent data of Remp et al. (9) on the copolymerization of poly(ethylene oxide) macromonomer with styrene appears to indicate a similar reduction of the macromonomer's reactivity as compared to a model monomer, although the reported scatter in r_1 values depending on the condition is puzzling for us to understand clearly at present.

Experimental

MEO-VB was prepared by the reaction of sodium alkoxide of 2-methoxyethanol with p-vinylbenzyl chloride (10), bp. 106–110°C/3 mmHg, and confirmed to be over 99 % pure by ¹H NMR and GPC. The preparation and the characterization of PEO-VB macromonomers, their copolymerization with styrene, and the product analyses were performed as described in detail in the previous paper (1).

Viscosities were measured with an Ubbelohde viscometer at $25 \pm 0.05^\circ\text{C}$ except for PEO-VB-93 in MIBK in which case $49 \pm 0.05^\circ\text{C}$ was chosen to ensure a clear solution.

Polymer-polymer compatibility test was made with a film prepared by casting on a glass plate from a benzene solution of a mixture (1/1 w/w) of polystyrene and poly(ethylene oxide). They were found to be incompatible to give an unclear or phase separated film as observed directly under a microscope (60X) on a micromelting point apparatus (Yanagimoto Co., Ltd.).

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