

EFFECT OF SOLVENT ON THE COPOLYMERIZATION OF 2,2,6,6-TETRAMETHYL 4-PIPERIDINYL METHACRYLATE WITH STYRENE

ZHAO Ruinian(赵瑞年) and LIANG Wenzhong(梁文忠)

(*Institute of Chemistry, Academia Sinica, Beijing*)

ABSTRACT

The radical copolymerizations of 2,2,6, 6-tetramethyl 4-piperidinyl methacrylate (TPM) with styrene in various solvents have been studied. The monomer reactivity ratios r_1 and r_2 were determined. It is observed that in all of these reaction systems, there are appreciable solvent effects on both r_1 and r_2 , which can be correlated to the difference in chemical shifts of olefinic protons of TPM. And the variance of the copolymer microstructure in various media was discussed.

The copolymer of 2,2,6, 6-tetramethyl-4-piperidinyl methacrylate (TPM) with styrene(St) is a novel polymeric hindered amine stabilizer for synthetic polymers with excellent performances. The copolymerization of TPM with styrene^[1-3], and the application of TPM-St copolymer stabilizer in the modification of polypropylene fibers have already been reported^[2]. In the present paper, the copolymerization of TPM with St was carried out in various solvents, e.g., benzene, chlorobenzene, dimethyl formamide, petroleum ether and pyridine. The copolymerization parameters were determined, the effect of solvent on monomer reactivity ratios and the copolymerization rate were studied. We found that in all of these systems, there are appreciable solvent effects on both r_1 and r_2 , which can be correlated to the difference in chemical shifts of olefinic protons of TPM. Also, the monomer unit sequence distribution along the copolymer chain, and the microstructure of the St-TPM copolymer were discussed.

EXPERIMENTAL

Materials

TPM is prepared according to the method described in detail previously^[3]. Styrene, and solvents, petroleum ether, benzene, chlorobenzene, pyridine and dimethyl formamide, and other reagents are chemically pure grade and were purified in the usual manner before use.

Polymerization

The copolymerizations were conducted in well-cleaned and dried polymerization tubes. Certain amounts of monomer, solvent and initiator were added into the tubes, purged with argon, degassed, and then the tubes were sealed under argon atmosphere. Polymerization reactions were carried out by keeping the tubes in a thermostat at 60°C for certain periods. The products were separated, purified and dried as described previously^[3].

Copolymer composition was determined from the carbon content of the elemental analysis data. ¹H NMR was recorded on a CAMECA RMN 250MHz high resolution nuclear magnetic resonance spectrometer, using tetramethyl silane as an internal reference.

RESULTS AND DISCUSSION

1. Effect of reaction medium upon monomer reactivity ratios

The radical copolymerization of $\text{St}(\text{M}_1)$ with $\text{TPM}(\text{M}_2)$ were carried out in petroleum ether(P), benzene(B), chlorobenzene(CB), pyridine(Py) and dimethyl formamide(DMF), respectively, with AIBN as the initiator. The monomer feed ratio and the copolymer composition are compiled in Table 1. The reactivity ratios r_1 and r_2 were determined based on the method of Kelen and Tüdös^[4]. According to the Alfrey-Price equation^[5], the Q and e values were calculated. These results are compiled in Table 2. The dielectric constants of the solvents are also shown.

It was observed that the monomer reactivity ratios varied appreciably with the reaction medium. In petroleum ether, the value of r_1 is close to that of r_2 , whereas those in benzene and DMF, the differences between them are relatively large. The value of Q_2 in benzene is the lowest while that in DMF, the strong polar solvent, is the highest. Thus, the reactivity of TPM in benzene is much lower than in DMF.

2. Correlation between r_1 and r_2 with the structure parameter of the monomer in various mediums

From Table 2, an approximately linear relationship between r_1 and r_2 with the dielectric constant of the solvents was obtained. But some data located apart from the straight line (see Fig. 1). Similar results were also reported in the literature^[6,7].

Ito et al.,^[8] have studied the IR spectra of methacrylic monomers in various solvents, and correlated r_1, r_2 with the absorbance shifts of $\text{C}=\text{C}$ and $\text{C}=\text{O}$, for the copolymerization system of styrene and methacrylic esters in various solvents. But there exists no linear relationship between r_1, r_2 with $\gamma_{\text{C}=\text{C}}$ and $\gamma_{\text{C}=\text{O}}$ for many other acrylic monomer copolymerization systems^[7,9].

We have investigated the effect of solvent on the NMR spectra of both monomers for the copolymerization system St-TPM, and the results are shown in Table 3. The variance of the difference in chemical shifts between olefinic protons for St in various solvents is relatively smaller than that for TPM. And substantially linear dependence of r_1, r_2 on the difference in chemical shifts between olefinic protons of TPM was found. (Fig.2)

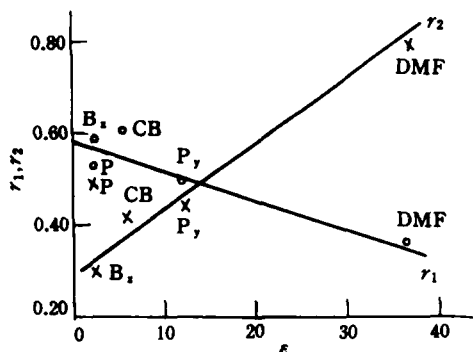


Fig. 1 Relationship between r_1, r_2 and dielectric constants of solvents.

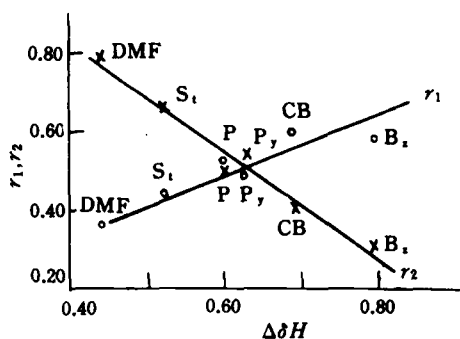


Fig. 2 Dependence of r_1, r_2 on the differences in chemical shifts($\Delta\delta\text{H}$)

3. Effect of solvent upon the rate of copolymerization

The copolymerization of St and TPM with different monomer feed compositions were conducted in benzene and DMF, respectively. The relationship between the copolymerization rate and monomer feed composition is shown in Fig.3. The results indicated that the copolymerization

Table 1 Copolymerization of St(M_1) with TMPM(M_2) in various solvents (60°C)^a

Solvent	X	f_1	Y	F_1
Petroleum ether	9.6860	0.9064	6.0147	0.8574
	3.3404	0.7696	2.3800	0.7041
	1.8047	0.6435	1.6020	0.6157
	1.1553	0.5360	1.0573	0.5739
	0.7317	0.4225	0.9088	0.4761
	0.3279	0.2469	0.4657	0.3177
	0.1522	0.1321	0.2615	0.2075
Benzene	4.4471	0.8164	3.3660	0.7710
	2.2413	0.6915	2.0013	0.6668
	1.4743	0.5958	1.5053	0.6008
	0.9083	0.4760	1.2024	0.5459
	0.7160	0.4174	0.9741	0.4934
	0.3681	0.2691	0.6574	0.3966
	0.2507	0.2004	0.5200	0.3421
Chloro- benzene	6.9334	0.8740	4.8846	0.8301
	3.5451	0.7800	2.8910	0.7430
	1.4467	0.5913	1.5483	0.6076
	0.8796	0.4680	0.9623	0.4904
	0.3431	0.2555	0.5358	0.3489
	0.2396	0.1932	0.4311	0.3012
Pyridine	4.9119	0.8308	3.1539	0.7593
	3.9851	0.7994	2.6170	0.7235
	1.9483	0.6608	1.5849	0.6131
	1.3052	0.5662	1.1819	0.5417
	0.9231	0.4800	0.9666	0.4915
	0.4162	0.2939	0.5432	0.3520
	0.2313	0.1879	0.4042	0.2879
DMF	4.8234	0.8283	2.5334	0.7170
	3.1379	0.7684	1.5400	0.6063
	1.6926	0.6286	1.1329	0.5312
	0.8081	0.4469	0.6481	0.3932
	0.4684	0.3119	0.4730	0.3211
	0.2698	0.2125	0.2787	0.2180
Styrene (Bulk)	5.3309	0.8420	3.5190	0.7787
	2.2746	0.6946	1.5372	0.6059
	1.7351	0.6344	1.2231	0.5502
	1.0483	0.5118	1.0000	0.5000
	0.6729	0.4022	0.6999	0.4117
	0.3999	0.3805	0.4176	0.2946

a) Total monomer concentration: 1.60 mol/L, AIBN: 1.60×10^{-2} mol/L $X = M_1/M_2$; $Y = m_1/m_2$; $f_1 = M_1/(M_1 + M_2)$; $F_1 = m_1/(m_1 + m_2)$

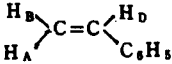
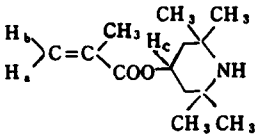
Table 2 Copolymerization parameters of St(M_1)-TMPM(M_2)^{a),b)}

Solvent	ϵ	r_1	r_2	$r_1 r_2$	Q_2	e_2
Petroleum ether	2.01	0.53	0.49	0.26	0.75	0.36
Benzene	2.28	0.58	0.30	0.17	0.61	0.53
Chlorobenzene	5.61	0.60	0.41	0.25	0.63	0.38
Pyridine	12.3	0.49	0.44	0.20	0.76	0.44
DMF	36.7	0.36	0.79	0.28	1.13	0.33
Styrene(Bulk)	2.43	0.44	0.60	0.26	0.91	0.35

a) Total monomer concentration: 1.60 mol/L AIBN: $1.60 \cdot 10^{-2}$ mol/L

b) $Q_1 = 1.0$, $e_1 = -0.80$

Table 3 Chemical shifts of olefinic protons for St and TMPM in various solvents (ppm)^{a),b)}

Solvent									
	δH_A	δH_B	$\Delta \delta H$	$\Delta \delta H_D$	δH_A	δH_B	$\Delta \delta H$	δH_C	$\delta H_{\alpha}-CH_3$
Petroleum ether	5.58	5.07	0.51	6.57	5.96	5.36	0.60	5.19	1.86
Benzene	5.58	5.05	0.53	6.56	6.10	5.31	0.79	5.28	1.90
Chlorobenzene	5.58	5.07	0.53	6.56	6.07	5.38	0.69	5.23	1.90
Pyridine	5.70	5.16	0.54	6.69	6.10	5.47	0.63	5.29	1.93
DMF	5.79	5.20	0.59	6.77	5.98	5.54	0.44	5.17	1.89
Styrene					6.06	5.54	0.52	5.23	1.89

a) Tetramethylsilane was used as an internal reference

b) $\Delta \delta H = \delta H_A - \delta H_B$, or $\delta H_A - \delta H_B$

have the rates intermediate between those of the homopolymerization of the individual monomers. But the rate is reduced to a much greater extent by the addition of a small amount of St to TMPM than that increased by the addition of a small amount of TMPM to St. Thus, the solvent effect is relatively large on the reactivity of TMPM, whereas the reactivity of St is substantially unaffected.

From Fig.3, we can see that the polymerization rates of St in both benzene and DMF are the same, while the polymerization rate of TMPM in DMF is almost three times that in benzene.

4. Dependence of copolymer microstructure on the reaction medium

According to the statistical method proposed by Harwood et al.^[10] the monomer unit sequence distribution along the copolymer chain and the Harwood run number (R), a parameter characterizing number-average alternating frequencies per one hundred monomer units, were determined for the copolymers obtained in various solvents. The number-average monomer unit sequence length ($\overline{L_n M_i}$) and Harwood run number for feed ratio equals unity and those for the

azeotropic copolymer are compiled in Tables 4 and 5, respectively. These data indicate that there is an appreciable effect on the microstructure of the copolymer for various reaction mediums.

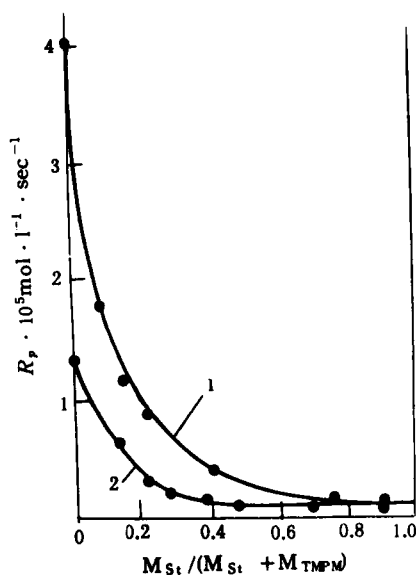


Fig. 3 Dependence of copolymerization rate on feed

1. DMF; 2. C_6H_6

Table 4 Number average sequence length ($\overline{L_n M_i}$) and Harwood run number (R) for $St(M_1)$ -TMPM copolymer ($M_1/M_2 = 1$; $60^\circ C$)

Solvent	$\overline{L_n M_1}$	$\overline{L_n M_2}$	R
Petroleum ether	1.49	1.53	66
Benzene	1.30	1.58	69
Pyridine	1.44	1.49	68
DMF	1.79	1.36	63
Styrene	1.60	1.44	66

Table 5 Number average sequence length ($\overline{L_n M_i}$) and Harwood run number (R) for $St(M_1)$ -TMPM azeotropic copolymers ($60^\circ C$)

Solvent	$\overline{L_n M_1}$	$\overline{L_n M_2}$	R
Petroleum ether	1.58	1.45	66
Benzene	1.97	1.18	63
Pyridine	1.54	1.40	68
DMF	1.12	3.39	44
Styrene	1.31	1.84	63

Since in all the cases studied, r_1 is less than one, thus M_1 radical will tend to add the other monomer unit TPM. However, there is a random aspect to copolymerization due to the

Table 6 Sequence length distribution for St(M_1)-TPM(M_2) copolymerization in petroleum ether
($M_1/M_2 = 1.06$; 60°C)

Sequence length		Mole Percent	
n	St	TPM	
1	64	68.5	
2	23	22	
3	8.3	6.8	
4	3	2.2	
5	1.1	0.7	

Table 7 Sequence length distribution for St(M_1)-TPM(M_2) copolymerization in benzene
($M_1/M_2 = 1.06$; 60°C)

Sequence length		Mole percent	
n	St	TPM	
1	62	78	
2	24	17	
3	9	4	
4	3.4	0.8	
5	1.3	0.2	

Table 8 Sequence length distribution for St(M_1)-TPM(M_2) copolymerization in DMF
($M_1/M_2 = 1.06$; 60°C)

Sequence length		Mole percent	
n	St	TPM	
1	72	57	
2	20	25	
3	5.6	11	
4	1.7	4.5	
5	0.4	3	

probabilistic nature of the reaction. The microstructure of St-TMPM copolymer is described by the distributions of various length of the M_1 and M_2 sequences, that is, the sequence-length distribution. According to the classical method^[11], the mole percent of forming M_1 and M_2 sequences of length n is determined. The results are compiled in Tables 6—8. It is clear that the copolymers with the feed ratio approximately equal unity, and possess microstructures which are very different from that of an perfectly alternating copolymer. And they varied with the nature of the reaction medium.

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