Initiation Step of Radical Polymerization of Styrene in Various Non-Aromatic Solvents

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ABSTRACT: Rates of initiation of radical polymerizations (R_i) of styrene by several initiators in non-aromatic solvents were determined and compared with those in benzene. It is considered that by forming π-complex with a geminate radical, benzene suppresses cage recombination when both are bulky, but assists it when one is small. But non-aromatic solvents show only viscosity effect and are considered to be inert-solvents.

KEY WORDS   Initiation Rate / Initiation Efficiency / Tempol / Inhibitor Method / Aromatic Effect / Non-Aromatic Solvent / Cage Recombination /

Previousely we reported the dependence of initiation efficiency (f) in radical polymerization of styrene (St) with azobisisobutyronitrile (AIBN) in several aromatic solvents on the viscosity of the system and monomer concentration.[1] The viscosity dependence of f was reported by Schulz et al.[2] and Smets et al.[3] as cage effect. However we found marked deviation of f in carbontetrachloride[4] from the relation with viscosity.[1]

To clarify the marked deviation, we carried out radical polymerizations of St with AIBN in various non-aromatic solvents and determined rate of initiation (R_i) by several methods. Then radical polymerizations of St with peroxides in benzene and cyclohexane were carried out and R_i were estimated on the basis of R_p (rate of polymerization) and known k_t/k_p^2.

EXPERIMENTAL

Benzene, cyclohexane, cyclohexanol, cyclo-hexanone, hexane, carbontetrachloride, methanol, and tetrahydrofuran (THF) were used as solvents. These solvents, St, AIBN, p-benzoquinone (BQ), and 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (Tempol) were commercially obtained and purified by oridinal methods. Benzoyl peroxide (BPO), cumyl hydroperoxide (CHP), t-butyl hydorperoxide (BHP), p-menthanhydroperoxide (MHP), dicumyl peroxide (DCP), di-t-butyl peroxide (DTBP), t-butyl cumyl peroxide (BCP) were used as initiators without further purification.

Fixed amounts of St, initiator and solvent were charged into a Pyrex glass tube or dilatometer and degassed by freezing, pumping, and thawing. After sealing under vacuum, polymerization was carried out at 60°C. R_p was determined gravimetrically. R_i were estimated as follows: ① inhibition method using Tempol, ② inhibition method using BQ, ③ from R_p and k_t/k_p^2 obtained by $1/P_n$ vs. R_p plots, ④ from the decay speed of Tempol measured by ESR with JEOL JES-FE3XG.

The decomposition rate constant of AIBN was determined by following the volume of nitrogene produced as previously reported[5] and that of peroxide was determined by following concentration iodometrically. P_n of poly(St) were determined from the intrinsic viscosity $[\eta]$ measured in benzene at 30°C.

RESULTS AND DISCUSSION

Determination of R_i

Typical examples of R_i determination by the above 4 methods are shown in Figures 1—4, and R_i thus obtained in benzne, cyclohexane and n-hexane are listed in Table I.
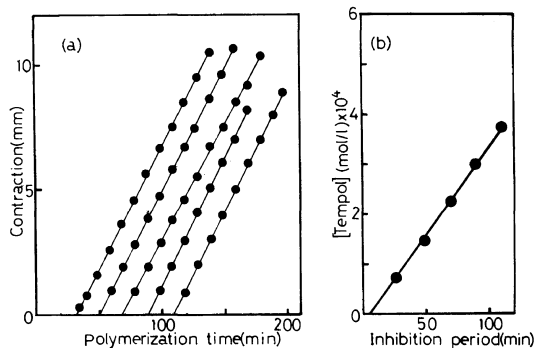

Figure 1. Measurements of inhibition periods by Tempol at 60°C (a) and plots of Tempol concentration against inhibition periods (b). Solvent, cyclohexane; [St] = 30 vt%: [AIBN] = 6.08 × 10⁻³ mol l⁻¹.
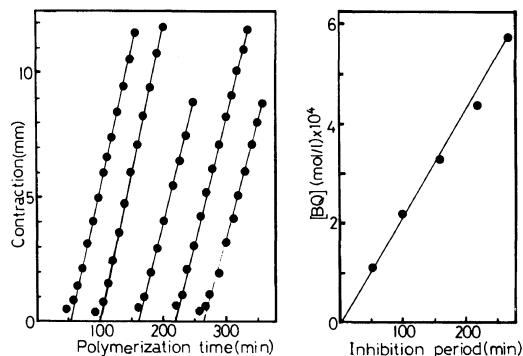

Figure 2. Measurements of inhibition periods by p-benzoquinone (BQ) at 60°C (a) and plot of BQ concentration against inhibition periods (b). Solvent, cyclohexane; [St] = 30 vol%; [AIBN] = 6.08 × 10⁻³ mol l⁻¹.

As shown in Table I, when a solvent is absent or is benzene, R_i obtained by these methods are in good agreement. However, R_i obtained using BQ in cyclohexane and n-hexane are smaller than those obtained by other methods, especially at low St concentration (Table I). Although BQ is used as a suitable inhibitor for St, BQ may not catch the primary radicals quantitatively in non-aromatic solvents. Therefore Tempol was used as the inhibitor in this study and R_i obtained by using Tempol in several non-aromatic solvents are listed in Table III.

Variation in k_d

To obtain f, k_d should be determined, and k_d in bulk, neat solvent and mixtures of St/solvent at 50/50 (v/v) were determined at 60°C by following the volume of nitrogen produced and listed in Table II. As shown in
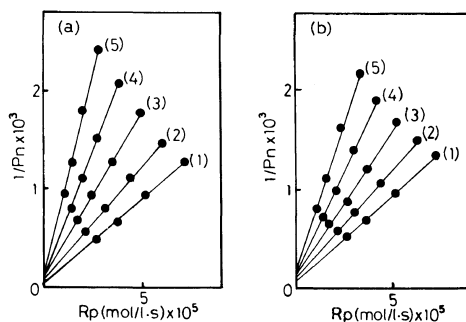

Figure 3. Plots of $1/P_n$ against R_p at 60°C in n-hexane (a) and cyclohexane (b). [St] vol%: 100, (1); 70, (2); 60, (3); 50, (4); 30, (5).
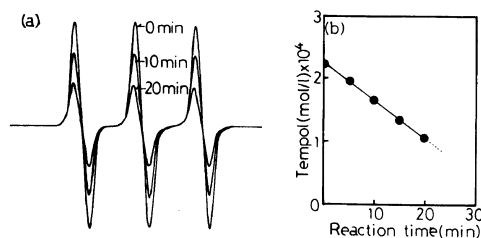

Figure 4. Variation in ESR signal of Tempol at 60°C (a) and plots of the Tempol concentration against the reaction time (b). Solvent, benzene; [St] = 80 vol%; [AIBN] = 6.08 × 10⁻³ mol l⁻¹.

Table I. $R_i{}^a$ with AIBN in benzene, cyclohexane and n-hexane determined by various methods at 60°C

Solvent	Method	R_i (mol l^{-1} s^{-1}) × 10^8 [St]/vol%							
		0	30	50	60	70	80	90	100
Benzene	①		7.14	8.17		8.50		9.16	9.36
	②		7.36	8.07	8.40	8.70			9.47
	③		7.6	8.1	8.4	8.7			9.5
	④	6.20	7.50	8.11	8.33	8.56	9.06		9.38
Cyclohexane	①		5.41	6.27		6.94		8.25	9.36
	②		4.40	5.70		6.90			9.47
	③		5.8	6.8	7.2	7.6			9.5
	④	2.00	5.40	6.13	6.63	6.98	7.39	8.13	9.38
n-Hexane	①		5.67	6.78		7.72		8.50	9.36
	②			4.70	5.30	6.50	7.40		9.47
	③			6.3	7.0	7.4			9.5
	④	1.80	6.10	7.14	7.29	7.78		8.72	9.38

[a] [AIBN] = 6.08×10^{-3} mol l^{-1}. Experimental error, $ca. \pm 3\%$.

Table II. Values of $k_d{}^a$ of AIBN in various solvents at 60°C

Solvent	$k_d \times 10^5$ s^{-1}
St	1.06
Benzene	1.14
St/benzene[b]	1.08
Cyclohexane	1.03
St/cyclohexane[b]	1.03
n-Hexane	1.05
St/methanol[b]	1.21
St/THF[b]	1.40
St/cyclohexanone[b]	1.15
St/cyclohexanol[b]	1.26
St/n-Hexane[b]	1.05

[a] Experimental error, $ca. \pm 3\%$.
[b] Mixing ratio, 50/50 (v/v).

Table III. R_i and f by AIBN in the mixture of St/solvent (50/50 v/v) and viscosity (η) of the mixture at 60°C

Solvent	$R_i{}^a$ (mol l^{-1} s^{-1}) × 10^8	f	η/cP
Benzene	8.17	0.62	0.43
n-Hexane	6.78	0.55	0.32
Methanol	7.20	0.49	0.38
THF	8.32	0.49	0.42
Cyclohexane	6.27	0.48	0.48
Cyclohexanone	5.68	0.40	1.63
Cyclohexanol	4.74	0.31	2.71

[a] [AIBN] = 6.08×10^{-3} mol l^{-1}. Experimental error, $ca. \pm 3\%$.

Table II, variation in k_d was not so large and k_d in the mixture were almost the average of those in bulk and in neat solvents. So the values at the other mixing ratio were estimated by proportional distribution, and used for estimation of f.

Solvent Effects on R_i and f

R_i in the mixture of St/solvent (50/50 (v/v)) are listed in Table III. As shown in Table III, R_i in these solvents are smaller than in benzene but not in THF and large values in THF are caused by large k_d. The values of f were caluculated from R_i and k_d, and are listed in Table III. As shown in Table III, f in non-aromatic solvents are smaller than in benzene.

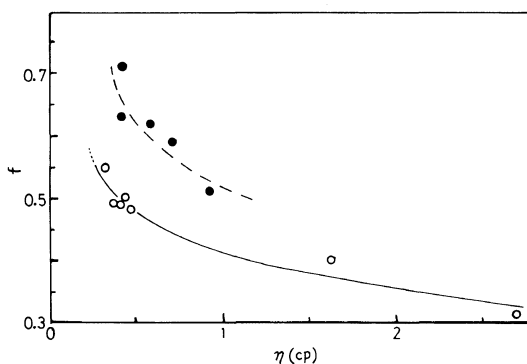The values of f are plotted against viscosity of St/solvent mixture in Figure 5. As shown in

Figure 5. Relation between f and η in various solvents at 60°C. ○, non-aromatic solvent; ●, aromatic solvent. [St] = 4.36 mol l^{-1} (50 vol%).

Figure 6. Dependence of R_i on monomer concentration in cyclohexane (a), n-hexane (b), and benzene (c) at 60°C. [AIBN] = 6.08 × 10^{-3} mol l^{-1}.

the figure, f decreased with increasing viscosity of the mixture, making a curve almost parallel to that found in aromatic solvents. These similar curves indicate that there is no marked difference between the viscosity dependence of f in aromatic solvents and in non-aromatic solvents. Carbonyl compounds such as cyclohexanone did not show different influence from the other non-aromatic solvents. Hence much difference between two curves may be caused by aromatic effect.

We consider the effect as follows: Even one geminate radical makes a π-complex with an aromatic solvent molecule, as another radical may move in a different direction within the complexing time, geminate radicals have fewer chances to encounter each other, cage recombination should be suppressed in aromatic solvents, and high efficiency results in aromatic solvents. On the other hand, a non-aromatic solvent molecule does not make a complex, geminate radicals may rebound without time lag, and they have more chances to encounter each other, cage recombination should be enhanced in non-aromatic solvents, and lower efficiency results in non-aromatic solvents.

Concentration Dependence of R_i

R_i obtained using Tempol in benzene, cyclohexane and n-hexane at several St concentrations (Table I) are plotted against
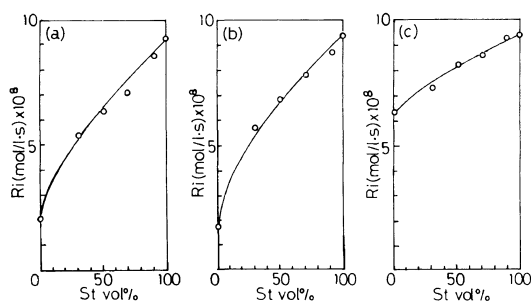
monomer concentration in Figure 6. As shown in the figure, R_i decreases with increasing solvent from the value in bulk to that in neat solvent gradually in benzene and remarkably in cyclohexane or n-hexane. Variation in k_d with monomer concentration is not so large. Thus, variation in R_i is caused by that in f with monomer concentration.

In the figure, results in a neat solvent were obtained by method ④, because R_i in the absence of monomer could not be determined by the above methods (①—③). Although $R_i = 0$ in a neat solvent theoretically, the values were estimated by measuring the rate of decay of Tempol with ESR (method ④) and are hypothetical or limiting values. The values are considered to be the rate of free radical production from geminate radical. The difference between the value in neat benzene and in neat cyclohexane or neat hexane is considered the aromatic effect. Then the difference between the value in bulk and that in neat benzene is considered to be the monomer effect, and St has both aromatic and monomer effects. R_i dependence on [St] appeared as a combination of these effects.

Polymerization with Peroxide

R_p obtained in benzene and cyclohexane using various peroxides at 60°C are listed in Table IV. Of course they were obtained by deduction of pure thermal polymerization rate from total polymerization rate. R_i were

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Table IV. $R_p{}^a$ and $R_i{}^b$ with various peroxides in benzene and cyclohexane at 60°C

Initiator		R_p (mol l^{-1} s^{-1}) × 10^6		R_i (mol l^{-1} s^{-1}) × 10^9	
	[I] (mol l^{-1}) × 10^2	Benzene	Cyclohexane	Benzene	Cyclohexane
AIBN	0.62	24.53	23.08	77.7	67.4
CHP	1.86	4.56	6.93	2.69	6.07
BHP	1.84	3.57	3.76	1.65	1.80
MHP	1.83	5.18	5.49	3.50	3.82
DCP	1.82	2.14	2.10	0.59	0.56
DTBP	1.82	1.36	1.26	0.24	0.20
BPO	0.86	14.88	19.47	28.7	48.0
BCP	1.83	2.37	2.09	0.73	0.55

a [St] = 4.36 mol l^{-1} (50 vol%).
b Derived from R_p and $k_t/k_p{}^2$ (1230 for benzene, 1200 for cyclohexane).

Table V. Values of k_d of BPO and CHP in benzene and cyclohexane at 60°C^a

	k_d in benzene	k_d in cyclohexane
BPO	0.22×10^{-5} (s^{-1})	0.95×10^{-5} (s^{-1})
CHP	0.60×10^{-7} (s^{-1})	0.50×10^{-5} (s^{-1})

a These values were determined iodometrically in the absence of styrene.

calculated from R_p and $k_t/k_p{}^2$ (1230 for benzene and 1200 for cyclohexane) and are listed in Table III. As shown in Table IV, when hydroperoxide was used, R_i in cyclohexane was larger than in benzene, but with di-peroxide except BPO, R_i in benzene was larger than in cyclohexane.

The values of k_d of the peroxides were not obtained in the presence of St at 60°C. Thus, it is difficult to discuss differences between R_i in benzene and cyclohexane. However, k_d of BPO and CHP could be determined in neat benzene and cyclohexane and are listed in Table V. Variation in R_i is discussed on the basis of k_d.

We assumed the following: (a) The influence of St on k_d of peroxide is similar in benzene and cyclohexane. (b) Variation in k_d of other di-peroxides with a solvent is similar to that of BPO. (c) Variation in k_d of other hydroperoxides is similar to that of CHP. Thus, when di-peroxide is used as an initiator, f in benzene

is larger than that in cyclohexane. When hydroperoxide is used as an initiator, f in benzene is smaller than in cyclohexane. We considered the reason as follows: When di-peroxide which produces bulky radicals is used, bulky radicals do not diffuse so fast but benzene retards cage recombination. When hydroperoxide which produces a bulky radical and a small hydroxyl radical is used, the small radical cannot diffuse faster in benzene than in cyclohexane because of π-complex formation.

CONCLUSION

Aromatic solvents play important roles in addition to viscosity effect in the initiation step of radical polymerization of styrene. When geminate radicals are bulky, aromatic solvents suppress the cage recombination by forming a π-complex with the radicals. But, when the geminate radicals are as small as the hydroxyl radical, solvents assist cage recombination by retarding rapid diffusion.

Non-aromatic solvents do not play such special roles, but show only viscosity effect and should be considered inert-solvents.

Styrene shows aromatic and monomer effects, and R_i dependence on monomer concentration is caused by variation in these effects.

The size of the primary radical is an important factor in the initiation step.

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