Equilibrium Polymerization of Acenaphthylene and Its Copolymerizations with Electron-Accepting Vinyl Monomers

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ABSTRACT: Radical polymerization kinetics of acenaphthylene in toluene using 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator was investigated revealing an equilibrium polymerization. The values of monomer concentration at equilibrium were determined to be between 1.3 and 3.3 mol/L for a temperature range of 50–70 °C. The thermodynamic parameters were determined and showed an enthalpy change of $\Delta H = -43$ kJ/mol and an entropy change of $\Delta S = -98$ J/K·mol. Furthermore, copolymerization of acenaphthylene with electron-accepting vinyl monomers such as methyl methacrylate (MMA) and acrylonitrile (AN) were carried out and showed a change from random to alternating copolymerization as the acenaphthylene concentration decreased. This change in mechanism is rationally explained in terms of the equilibrium polymerization of acenaphthylene.

Introduction

In general, 1,2-disubstituted ethylenes are less reactive compared to 1,1-disubstituted and monosubstituted ethylenes due to steric hindrance of the 1,2-substituents in the transition state during propagation.[1] Although most do not homopolymerize, there are a few 1,2-disubstituted ethylenes which do homopolymerize, these include maleimides,[2] vinylene carbonate,[3] fumarates,[4] and acenaphthylene.[5]

Previously we reported that *N*-phenylmaleimide (PMI) undergoes an equilibrium polymerization when 2,2′-azobis(isobutyronitrile) (AIBN) is used as an initiator.[6] During these polymerizations, the equilibrium monomer concentrations were determined for the reaction temperatures. From these equilibrium monomer concentrations, the thermodynamic parameters were estimated. In the same report, we noted that, during copolymerization with phenyl vinyl sulfide (PVS), a change in mechanism occurred. As the PMI concentration decreased, the mode of polymerization changed from random to alternating, indicating the important role of PMI's equilibrium polymerization in determining its copolymerization fashion.

The work presented here describes the radical polymerization kinetics of acenaphthylene in toluene using AIBN as an initiator and the copolymerization behavior with the electron-accepting vinyl monomers such as methyl methacrylate (MMA) and acrylonitrile (AN).

Experimental Section

Materials. Acenaphthylene was repeatedly recrystallized from a mixture of ethanol and water (4:1 by volume) and dried under reduced pressure. Methyl methacrylate (MMA) and acrylonitrile (AN) were distilled under reduced pressure prior to use. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Toluene was washed with sulfuric acid, water, 5% aqueous sodium hydroxide solution, and again water; dried over sodium metal chips; and distilled.

Homopolymerization Kinetics. Given amounts of acenaphthylene, AIBN as an initiator, and toluene as a solvent were placed in an ampule, which was degassed completely by the freeze–thaw method (repeated three times) and sealed. The ampule was set in a bath thermostated at 50, 55, 60, 65, or 70 °C for time of polymerization and then opened. The concentration of acenaphthylene was determined spectrophotometrically with an absorption band of 324 nm. The polymerization rate (R_p) was calculated from the amounts of the monomer consumed for time of polymerization.

Copolymerization Procedure. Given amounts of acenaphthylene, MMA, or AN as a comonomer, AIBN, and toluene were placed in an ampule, which was degassed completely by freeze–thaw method (repeated three times) and sealed. The ampule was placed in a bath thermostated at 60 °C for time of polymerization and then opened. The reaction mixture was poured into an excess of hexane to precipitate the copolymer. For purification, the copolymer obtained was dissolved in a small amount of dichloromethane and the resulting solution was poured into an excess of hexane to precipitate the copolymer again. This dissolution–precipitation procedure was twice repeated. The copolymer was dried under reduced pressure until a constant weight was achieved.

Copolymer composition was established by elemental analysis. Number-average molecular weight ($\bar{M}_n$) of the copolymer was determined by gel permeation chromatography (GPC) using tetrahydrofuran and standard polystyrenes as an eluent and references, respectively.

Results and Discussion

Equilibrium Polymerization of Acenaphthylene. The UV–visible spectrum of acenaphthylene in toluene exhibited characteristic absorption band at 324 nm as shown in Figure 1, which was worth measuring concentration of acenaphthylene. The time–conversion plots for the polymerization of acenaphthylene with monomer concentration of 0.066 mol/L at 50, 60, and 70 °C are shown in Figure 2, where the plots obtained substantially form straight lines passing the origin, indicating that it shows no induction period. Polymerization rates (R_p's) were calculated from their slope.

A log–log plot of R_p versus initiator concentration ([AIBN]) at 60 °C displayed a good straight line with a slope of one-half as shown in Figure 3, indicating that the radical polymerization of acenaphthylene satisfactorily follows a square-root dependence of polymerization rate on initiator concentration similar to a conventional radical vinyl polymerization. A log–log plot of R_p versus monomer concentration of acenaphthylene is shown in Figure 4, where it displays a broken straight line, one part with a slope of unity in the acenaphthylene monomer concentration range above 0.06 mol/L and the other with a slope of about one-half in the acenaphthylene monomer concentration range below 0.06 mol/L. In the case of the high

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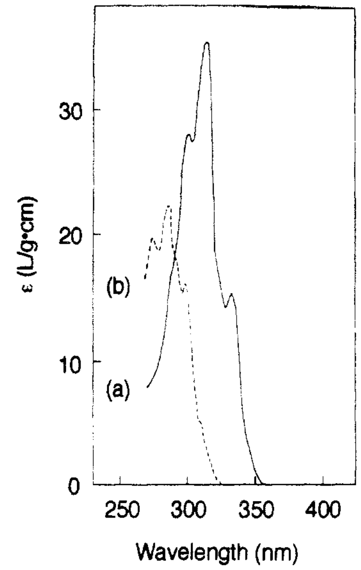

Figure 1. UV–vis spectra of (a) acenaphthylene and (b) poly(acenaphthylene) in toluene.

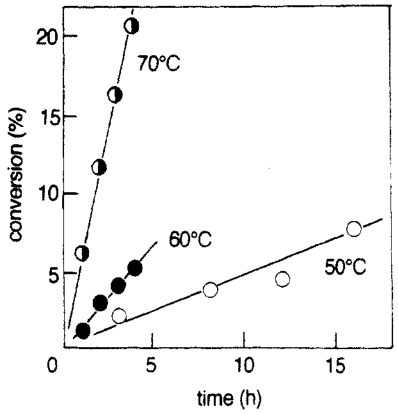

Figure 2. Time–conversion curves for the polymerization of acenaphthylene at various temperatures of (○) 50, (●) 60, and (◑) 70 °C. [Acenaphthylene] = 0.066 mol/L; [AIBN] = 1.1 × 10^{-2} mol/L.

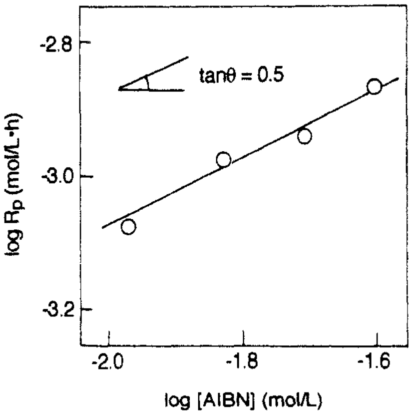

Figure 3. Plot of log R_p versus log [AIBN] for the polymerization of acenaphthylene at 60 °C. [Acenaphthylene] = 0.064 mol/L.

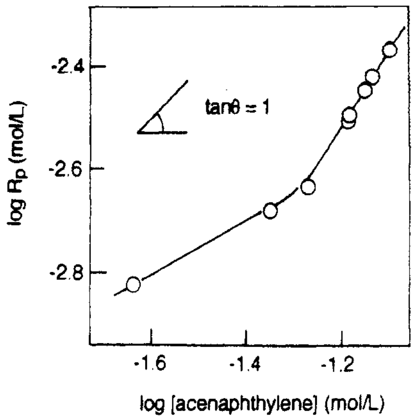

Figure 4. Plot of log R_p versus log [acenaphthylene] for the polymerization of acenaphthylene at 70 °C. [AIBN] = 1.1 × 10^{-2} mol/L.

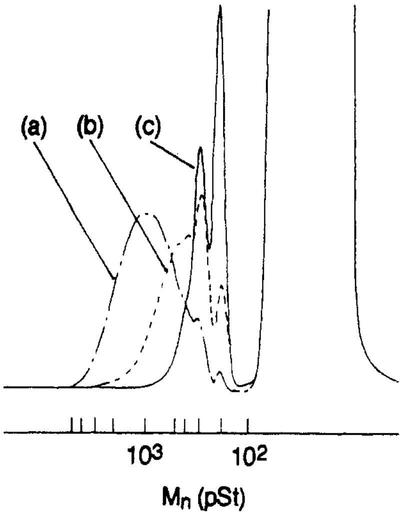

Figure 5. GPC chromatograms of the reaction mixtures at various monomer concentrations of (a) 0.07, (b) 0.04, and (c) 0.02 mol/L.

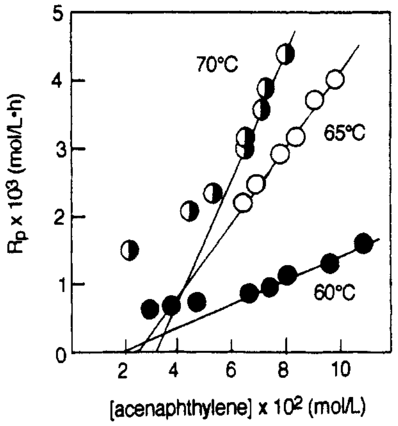

Figure 6. Plots of R_p versus [acenaphthylene] for homopolymerization of acenaphthylene in toluene at (●) 60, (○) 65, and (◑) 70 °C. [AIBN] = 1.1 × 10^{-2} mol/L.

monomer concentration a first-order dependence of R_p on monomer concentration is applicable to it as well as a conventional radical vinyl polymerization, whereas in the case of the low monomer concentration this conventional dependence of R_p would fail, implying that reactions other than the forward propagation would take part in polymerization. Figure 5 shows each gel permeation chromatograms for the reaction mixtures with feed monomer concentrations of 0.07, 0.04, or 0.02 mol/L at 70 °C for reaction time of 2 h. When the monomer concentration was as high as 0.07 mol/L, the reaction mixture consisted of no compound other than monomer and polymer. On the other hand, when the monomer concentration was reduced to 0.04 or 0.02 mol/L, it contained a considerable amount of low molecular weight products in addition to polymer and monomer. Reaction for the low molecular weight products could possibly render the polymerization rate out of the first-order dependence on monomer concentration. The low molecular weight products were investigated by GPC to have molecular weight of 200 or 400, corresponding to compounds of one or two monomer units, respectively. However, exact chemical structures

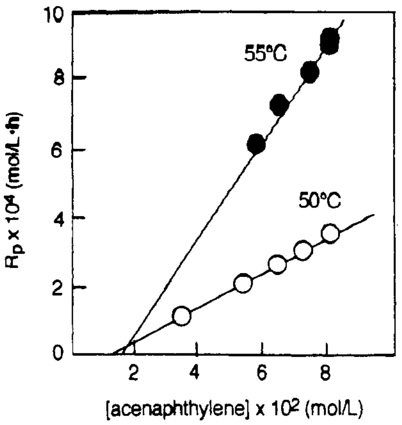

Figure 7. Plots of R_p versus [acenaphthylene] for homopolymerization of acenaphthylene in toluene at (○) 50 and (●) 55 °C. [AIBN] = 1.1 × 10^{-2} mol/L.

Table I. Equilibrium Monomer Concentration of Acenaphthylene ($[M]_e$)

temp, °C	$[M]_e \times 10^2$, mol/L	temp, °C	$[M]_e \times 10^2$, mol/L
50	1.3	65	2.5
55	1.6	70	3.3
60	2.0		

for them were unknown at the moment. Anyhow, at least in the region where the product consisted of mainly polymer with a negligibly small amount of low molecular weight products, polymerization of acenaphthylene was reasonably allowed to be treated according to the conventional kinetics of radical polymerization reaction.

Values of equilibrium monomer concentration were determined according to the method[7] of Vofsi and Tobolosky in which R_p's were plotted against monomer concentration as shown in Figures 6 and 7, where the extrapolation of the straight parts in the high monomer concentration region to the rate of zero permitted us to estimate an equilibrium monomer concentration of acenaphthylene ($[M]_e$), as summarized in Table I.

The relationship between $[M]_e$ and a reciprocal of the ceiling temperature ($1/T_c$) was given by the equation[8]

$$\ln [M]_e = \Delta H/RT_c - \Delta S/R \qquad (1)$$

where ΔH and ΔS are enthalpy and entropy changes for polymerization, respectively, and R is the gas constant. The linear relationship between $\ln [M]_e$ and $1/T_c$, as shown in Figure 8, allowed the values of enthalpy and entropy changes for polymerization of acenaphthylene to be ΔH = −43 kJ/mol and ΔS = −98 J/K·mol, respectively. Joshi reported ΔH of −67 kJ/mol for acenaphthylene by calorimetry of its radical polymerization in dichlorobenzene.[5] The ΔH value for the polymerization of acenaphthylene was found to be a little bit lower than that of styrene reported to be −73 kJ/mol,[9] probably being attributable to a steric hindrance effect of the 1,2-disubstitution. The ΔS value of acenaphthylene obtained in this experiment is within the range of 100–120 J/K·mol for conventional vinyl monomers.[1] It was thought therefore that the values of the thermodynamic parameters for the polymerization of acenaphthylene obtained from this way are quite reasonable.

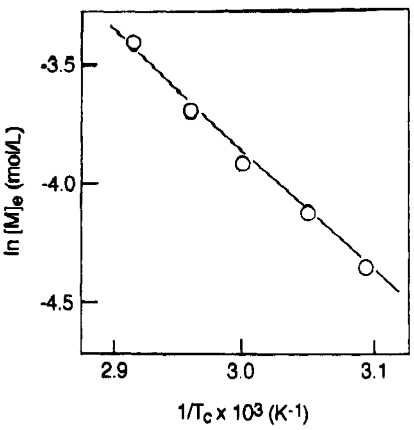

Figure 8. Plot of ln $[M]_e$ versus $1/T$ for polymerization of acenaphthylene.

Copolymerizations of Acenaphthylene with MMA and AN. Copolymerizations of acenaphthylene (M_1) with methyl methacrylate (MMA) (M_2) were carried out in toluene at 60 °C under a fixed acenaphthylene monomer concentration of 1.5 mol/L, much higher than the equilibrium monomer concentration of 0.02 mol/L at 60 °C. It was then reasonably thought that they took place without influence of depolymerization. The results are summarized in Table II and the copolymerization composition curve is shown as a line of closed circles in Figure 9. The results were successfully treated according to the cross section[10] and the Kelen–Tüdös[11] methods as shown as a line of closed circles in Figure 10, where a very straight line was given, indicating that the copolymerization satisfactorily follows the conventional terminal unit model copolymerization equation of Mayo and Lewis[10] and of Alfrey and Goldfinger.[12] The monomer reactivity ratios (MRR's) were given as r_1 = 1.6 ± 0.5 and R_2 = 0.36 ± 0.20

Table II. Copolymerizations of Acenaphthylene with MMA in Toluene at 60 °C[a]

	monomer feed						copolymer compound			
							anal., %			
run	Ace (M_1), mg	MMA (M_2), mg	Ace, mol %	toluene, mL	time, h	conversion, %	H	C	Ace,[b] mol %	$\bar{M}_n/10^3$ [c]
				[Ace] = 1.5 mol/L						
1	228.4	64.1	70.1	1	3	10.3	5.37	90.25	81.7	10
2	227.8	161.2	49.7	1	2	8.0	5.70	86.40	67.7	12
3	228.6	152.0	48.3	1	3	10.9	5.72	86.63	65.0	13
4	228.0	368.0	29.0	1	2	7.4	6.38	80.83	49.7	21
5	227.9	611.3	19.7	1	1	6.8	6.90	75.48	34.7	32
6	228.3	1353.9	10.0	1	1	5.4	7.49	68.16	16.9	90
				[Ace] = 0.04 mol/L						
7	231.5	68.6	68.9	38	72	0.7	5.82	86.55	68.2	2.3
8	121.7	87.6	47.8	20	72	4.1	6.36	81.42	51.5	2.8
9	152.2	150.1	40.0	25	48	6.8	6.77	80.19	47.8	2.8
10	152.0	186.9	34.9	20	20	8.2	6.31	79.68	46.3	3.9
11	60.8	165.4	19.5	10	15	9.5	7.07	75.35	34.4	5.8
12	30.3	181.6	9.9	5	2	9.8	7.44	69.43	19.8	5.8

[a] AIBN; 15 mg for runs of nos. 1–6, 40 mg for runs of nos. 7–10, and 10 mg for runs of nos. 11 and 12. [b] Calculated from C%. [c] Determined by GPC.

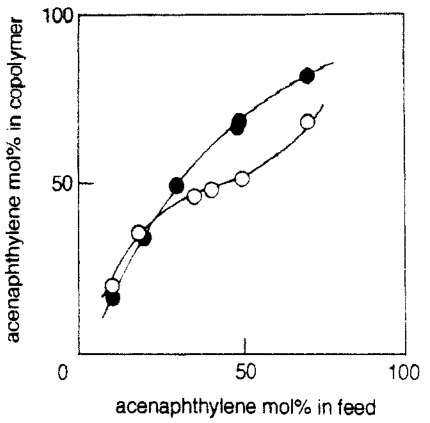

Figure 9. Copolymer composition curves of acenaphthylene with MMA in toluene at 60 °C: (●) [acenaphthylene] = 1.5 mol/L; (○) [acenaphthylene] = 0.04 mol/L.

at 60 °C, from which the Alfrey–Price Q–e values of acenaphthylene were calculated to be $Q = 1.5$ and $e = -0.63$. It is obvious that acenaphthylene is more highly reactive and less electron donating then styrene. Ballesteros et al.[13] and Noma et al.[14] reported MRR's of copolymerization of acenaphthylene with MMA as $r_1 = 1.05$, $r_2 = 0.36$ at 70 °C in dichlorobenzene and $r_1 = 2.25$, $r_2 = 0.44$ at 60 °C in benzene, respectively.

Copolymerizations of acenaphthylene (M_1) with acrylonitrile (AN) (M_2) were carried out in toluene at 60 °C under a fixed acenaphthylene monomer concentration of 2.0 mol/L, much higher than the equilibrium monomer concentration at 60 °C. The results are summarized in Table III and the copolymerization composition curve is shown as a line of closed circles in Figure 11. The results were successfully treated according to the cross section and the Kelen–Tüdös methods as shown as a line of closed circles in Figure 12, where a good straight line was given. The MRR's were given as $r_1 = 2.1 \pm 0.3$ and $r_2 = 0.0$ at 60 °C. Noma et al. reported MMR's of copolymerization of acenaphthylene with AN to be $r_1 = 2.56$ and $r_2 = 0.02$ at 60 °C in benzene.[14]

Influence of Acenaphthylene Monomer Concentration on Copolymerization Fashion. Copolymerizations of acenaphthylene with MMA or AN in toluene with AIBN at 60 °C were carried out in various amounts of toluene under the fixed monomer feed of 1:1 in order to look into the influence of the acenaphthylene monomer concentration on the propagations determining the copolymer composition. The results are summarized in Table IV. It was found in both copolymerization systems as shown in Figure 13 that the acenaphthylene monomer unit component percentages of the copolymers kept unchanged in the acenaphthylene monomer range above 0.5 mol/L, began to decrease gradually up to 50 mol % with decrease in acenaphthylene monomer concentration less than 0.5 mol/L, and finally no copolymers were obtained in the low acenaphthylene monomer concentration below 10^{-2} mol/L.

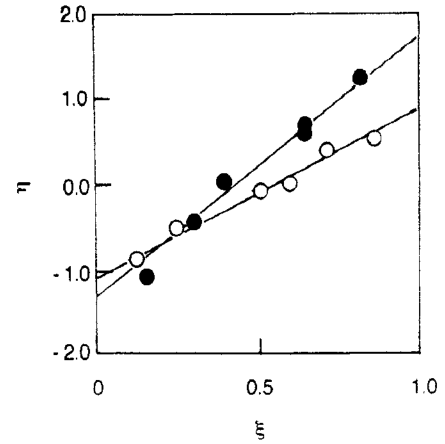

Figure 10. Kelen–Tüdös plots for the copolymerization of acenaphthylene with MMA in toluene at 60 °C: (●) [acenaphthylene] = 1.5 mol/L; (○) [acenaphthylene] = 0.04 mol/L.

Copolymerizations of acenaphthylene (M_1) with MMA (M_2) were carried out in toluene at 60 °C with an acenaphthylene monomer concentration of 0.04 mol/L, conceivably having a considerable amount of influence of depolymerization because it was close to the equilibrium monomer concentration. The results are summarized in Table II and the copolymerization composition curve is shown as a line of open circles in Figure 9. Obviously, its copolymerization fashion tended toward alternating compared to the copolymerization with the high acenaphthylene monomer concentration. The Kelen–Tüdös plot gave a good straight line as shown as a line of open circles in Figure 10, indicating no deviation from the terminal model copolymerization equation, and it allowed us to

Table III. Copolymerizations of Acenaphthylene with AN in Toluene at 60 °C[a]

							copolymer compound				
	monomer feed						anal., %				
run	Ace (M_1), mg	AN (M_2), mg	Ace, mol %	toluene, mL	time, h	conversion, %	H	C	N	Ace,[b] mol %	$\bar{M}_n/10^3$ [c]
				[Ace] = 2.0 mol/L							
1	609.0	24.5	89.7	2	5	8.5	5.27	94.18	0.55	94.3	8.0
2	609.2	97.5	68.5	2	4	10.8	5.26	93.37	1.51	85.2	8.4
3	608.4	144.5	59.5	2	3	6.9	5.22	92.69	2.69	80.2	8.6
4	609.1	216.1	49.6	2	3	7.0	5.26	92.37	2.36	78.0	8.4
5	609.0	319.8	39.9	2	3	6.1	5.26	91.49	3.26	71.2	10
6	609.2	495.3	31.3	2	2	4.7	5.31	90.57	4.13	65.3	9.6
7	609.1	855.3	19.9	2	2	3.2	5.22	89.70	5.08	59.4	12
8	609.1	964.4	18.0	2	1	2.4	5.32	89.37	5.32	58.0	11
				[Ace] = 0.03 mol/L							
9	228.3	34.1	70.0	50	72	1.0	5.77	91.37	2.86	71.0	1.4
10	228.3	53.7	59.7	50	72	2.8	5.66	90.64	3.71	66.1	1.4
11	123.6	48.7	46.9	27	72	3.0	5.75	89.10	5.15	59.0	1.4
12	182.4	98.1	39.3	40	40	11.6	5.57	89.00	5.43	57.4	1.4
13	159.9	129.9	30.3	35	40	9.5	5.66	88.41	5.93	54.6	1.6
14	114.1	159.7	19.9	25	40	9.8	5.55	88.27	6.19	53.2	1.6
15	45.9	143.3	10.0	10	20	9.0	5.69	86.93	7.38	47.3	1.6

[a] AIBN; 14 mg for runs of nos. 1–8, 40 mg for runs of nos. 9–13, and 10 mg for runs of nos. 14 and 15. [b] Calculated from C%. [c] Determined by GPC.

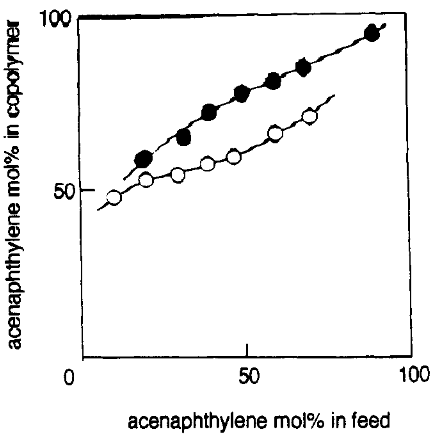

Figure 11. Copolymer composition curves of acenaphthylene with AN in toluene at 60 °C: (●) [acenaphthylene] = 2.0 mol/L; (○) [acenaphthylene] = 0.03 mol/L.

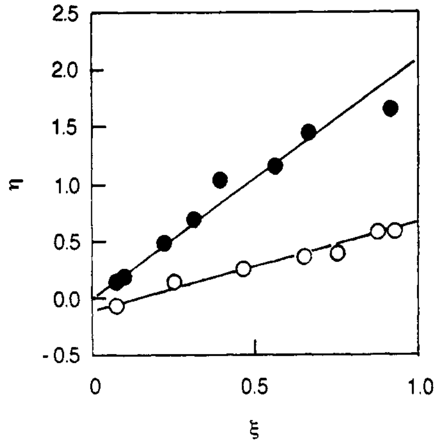

Figure 12. Kelen–Tüdös plots for the copolymerization of acenaphthylene with AN in toluene at 60 °C: (●) [acenaphthylene] = 2.0 mol/L; (○) [acenaphthylene] = 0.03 mol/L.

calculate MRR's as $r_1 = 0.8 \pm 0.4$ and $r_2 = 0.36 \pm 0.4$. It was worth noting that r_1 values remarkably decreased by one-half but r_2 values remained unchanged when the acenaphthylene monomer concentration decreased. This large decrease in r_1 was reasonably thought to be attributable to depolymerization in an equilibrium polymerization of acenaphthylene and also to let copolymerization fashion tend toward more alternating.

Furthermore, copolymerizations of acenaphthylene (M_1) with AN (M_2) were carried out in toluene at 60 °C with an acenaphthylene monomer concentration of 0.03 mol/L under a considerable influence of depolymerization. The results are summarized in Table III and the copolymerization composition curve is shown as a line of open circles in Figure 11. Obviously, the copolymerization took place in more alternating fashion compared to that of the high monomer concentration. The results were treated according to the cross section and the Kelen–Tüdös methods as shown as a line of open circles in Figure 12 to obtain the MRR's, $r_1 = 0.64 \pm 0.13$ and $r_2 = 0.02 \pm 0.01$. The copolymerizations of acenaphthylene with AN under two different acenaphthylene monomer concentrations were considered to be substantially similar to the corresponding copolymerizations of acenaphthylene with MMA.

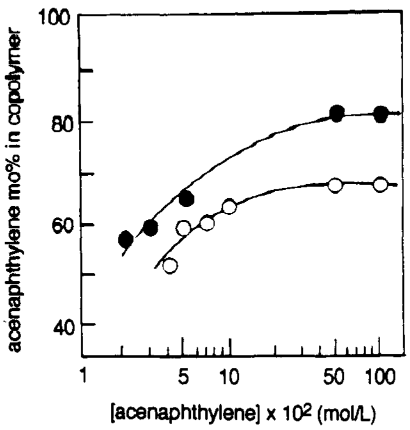

Figure 13. Influence of acenaphthylene monomer concentration on the composition of the copolymers of acenaphthylene with (○) MMA and (●) AN in toluene at 60 °C.

Copolymerization Mechanism. The change in copolymerization fashion with the acenaphthylene monomer concentration was rationally explained in terms of the reaction scheme reported previously.[15] The copolymerization of acenaphthylene (Ace) with comonomer (M_2) such as MMA or AN involves four kinds of propagations:

$$\sim\text{Ace}^\bullet + \text{Ace} \xrightarrow{k_{11}} \sim\text{Ace}^\bullet \tag{2}$$

$$\sim\text{Ace}^\bullet + \text{M}_2 \xrightarrow{k_{12}} \sim\text{M}_2^\bullet \tag{3}$$

$$\sim\text{M}_2^\bullet + \text{Ace} \xrightarrow{k_{21}} \sim\text{Ace}^\bullet \tag{4}$$

$$\sim\text{M}_2^\bullet + \text{M}_2 \xrightarrow{k_{22}} \sim\text{M}_2^\bullet \tag{5}$$

where k_{ij} is reaction rate constant for the propagation

Table IV. Copolymerizations of Acenaphthylene (M_1) with MMA or AN in Toluene at 60 °C

	monomer feed[a]							copolymer compound				
								anal., %				
run	Ace, mg	M_2, mg	toluene, mL	Ace, mol/L	AIBN, mg	time, h	conversion, %	H	C	N	Ace, mol %	$\bar{M}_n/10^3$ [b]
						M_2: MMA						
1	304.4	202.0	2	1.0	7	1	3.4	5.51	86.01		66.3[c]	10.0
2	230.0	151.7	2	0.75	7	2	3.1	5.80	86.06		66.5[c]	8.4
3	121.6	79.9	8	0.10	7	8	4.7	5.63	84.84		62.4[c]	2.8
4	128.3	86.0	12	0.07	40	48	12.1	6.12	83.34		57.5[c]	2.3
5	121.8	80.9	16	0.05	40	70	11.2	6.07	83.65		58.5[c]	2.3
6	122.0	87.6	20	0.04	40	72	8.2	6.36	81.42		51.5[c]	2.0
						M_2: AN						
7	152.2	53.8	1	1.0	7	5	9.6	5.50	92.45	2.04	80.2[d]	5.0
8	152.2	55.9	2	0.50	7	6	10.7	5.59	92.39	2.02	80.8[d]	3.3
9	121.5	42.5	16	0.05	40	70	9.3	5.94	89.80	4.27	64.4[d]	2.2
10	123.6	48.7	27	0.03	40	72	3.0	5.75	98.10	5.15	59.0[d]	2.0
11	121.4	42.5	40	0.02	40	72	4.1	5.63	89.07	5.30	56.7[d]	2.0

[a] Ace mol %, 50. [b] Determined by GPC. [c] Calculated from C%. [d] Calculated from N%.

between polymer radical with terminal monomer *i* unit and monomer *j*. The polymer radical with a terminal M_2 unit should react more readily with acenaphthylene than with MMA or AN (M_2) by taking account of general reactivity and polar effect between these monomers. In the case of the high acenaphthylene monomer concentration, the polymer radical with terminal acenaphthylene unit must be much more reactive with acenaphthylene than with M_2 because general reactivity of acenaphthylene is higher than that of MMA or AN. On the other hand, in the case of the low concentration of acenaphthylene, the polymer radical with the terminal acenaphthylene unit is no longer capable of reacting with acenaphthylene due to the great contribution of the depolymerization but it can react with M_2 with the assistance of polar effect between the two reacting species. Consequently, when acenaphthylene monomer concentration decreased much closer to the equilibrium monomer concentration, the copolymerization fashion was thought to be converted to the more alternating-like.

The change of the copolymerization fashion from random to more alternating in acenaphthylene–MMA and acenaphthylene–AN systems in the case of lowering the acenaphthylene monomer concentration was considered to be additional evidence for an equilibrium polymerization of acenaphthylene. From another viewpoint, it was noteworthy that whenever a monomer was carrying an equilibrium polymerization nature even slightly, its copolymerization had to suffer from a serious influence of its monomer concentration and its analysis could lead to a meaningless illusion without careful consideration of the monomer concentration.

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