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Polymerization Behavior of *N*,7,7-Tricyanobenzoquinone Methide Imine

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ABSTRACT: It was found that *N*,7,7-tricyanobenzoquinone methide imine (BMI) is homopolymerizable in toluene with 2,2′-azobis(isobutyronitrile) as an initiator under significant influence of depolymerization. The detailed study of its kinetics allowed us to determine its ceiling temperature, equilibrium monomer concentrations, and enthalpy (ΔH) and entropy changes (ΔS) of the polymerization, which are ΔH = 22.5 kJ/mol and ΔS = 38.1 J/K·mol. Its copolymerization with styrene took place always in an alternating fashion irrespective of polymerizable BMI monomer concentration, indicating that very strong electron donor–acceptor interaction between BMI and styrene plays an important role for determining copolymerization fashion. On the other hand, its copolymerization with highly conjugative, electron-accepting 7,8-bis(butoxycarbonyl)-7,8-dicyanoquinodimethane (BCQ) occurred in a random fashion to obtain monomer reactivity ratios, r_1(BMI) = 0.006 ± 0.005 and r_2 = 7.3 ± 2.0, at 60 °C.

Introduction

In a series of quinodimethane compounds, we have found that there are an interesting limited range of compounds such as 7,8-bis(alkoxycarbonyl)-7,8-dicyanoquinodimethanes,[1,2] 7,8-diacyl-7,8-dicyanoquinodimethanes,[3] and 7,8-bis(ethylthio)-7,8-dicyanoquinodimethane,[4] which are obtainable as crystal and are homopolymerizable with various initiators, and that they evidently undergo a typical equilibrium polymerization.[5] As their related compounds, we have recently prepared some novel quinone methide imine compounds such as *N*,7,7-tricyanobenzoquinone methide imine (BMI), *N*,11,11-tricyanonaphthoquinone methide imine (NMI), and *N*,15,15-tricyanoanthraquinone methide imine (AMI).[6] Among them only BMI is homopolymerizable with radical and anionic initiators even though its electron-accepting character is as strong as 7,7,8,8-tetracyanoquinodimethane (TCNQ).

In this paper, a radical polymerization of BMI was studied in detail to obtain thermodynamic parameters for polymerization of BMI and copolymerizations of BMI with styrene (St) and 7,8-bis(butoxycarbonyl)-7,8-dicyanoquinodimethane (BCQ) were carried out to determine their copolymerization fashion and the monomer reactivity of BMI.

Experimental Section

Materials. BMI[6] and BCQ[2] were prepared according to the methods of the previous papers. St was washed with 2% aqueous sodium hydroxide solution and water, dried over barium oxide, stirred with calcium hydride at room temperature for 6 h, and then distilled under reduced pressure. 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. Reagent-grade acetic acid was used without further purification.

Homopolymerization Kinetics. Given amounts of monomer, AIBN as an initiator, toluene as a solvent, and a drop of acetic acid as an anionic polymerization inhibitor were placed in an ampule, which was degassed completely by the freeze–thaw method and sealed. It was set in a bath thermostated at temperatures of 40, 50, 60, and 70 °C for the time of polymerization and then opened. The concentration of BMI was determined spectrophotometrically with an absorption band of 361 nm. The polymerization rate, R_p, was calculated from the amounts of the monomer consumed for fixed amounts of time.

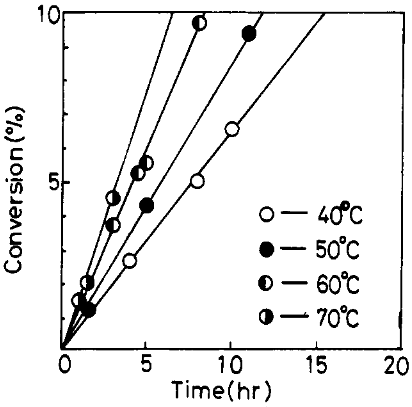

Figure 1. Time–conversion curves for the polymerization of BMI at various temperatures: 40 (○), 50 (●), 60 (◐), and 70 (◑) °C. [BMI] = 0.0395 mol/L; [AIBN] = 1.21 × 10^{-3} mol/L.

Copolymerization Procedure. Given amounts of monomers, AIBN, toluene, and a drop of acetic acid were placed in an ampule, which was degassed completely by the freeze–thaw method and sealed. The ampule was placed in a bath thermostated at temperatures of 40, 50, 60, and 70 °C for the time of polymerization and then opened. The reaction mixture was poured into excess isopropyl ether to precipitate the copolymer. For purification, the copolymer obtained was dissolved in a small amount of dichloromethane and the resulting solution was poured into excess hexane to precipitate the copolymer again. This procedure was repeated twice. The copolymer was dried under reduced pressure to constant weight.

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

Results and Discussion

Kinetics of Radical Polymerization. Relationships of the polymer yield versus time of polymerization, so-called time–conversion curves, for the homopolymerization of BMI at 40, 50, 60, and 70 °C are shown in Figure 1. The polymer yield increases linearly with the time of polymerization at these polymerization temperatures. A log–log plot of polymerization rate, R_p, versus initiator concentration, [AIBN], at 60 °C displays a good straight line with a slope of 0.49 as shown in Figure 2, indicating that the radical polymerization of BMI

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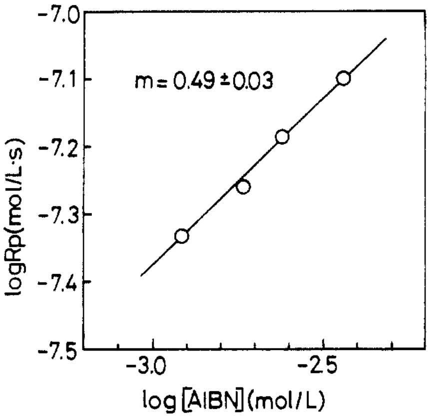


Figure 2. log–log plot of R_p versus [AIBN] for the polymerization of BMI at 60 °C. [BMI] = 0.0350 mol/L.

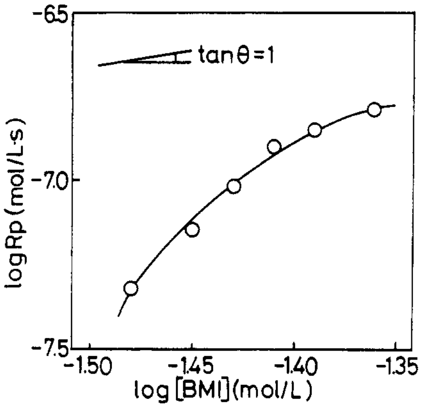


Figure 3. log–log plot of R_p versus [BMI] for the polymerization of BMI at 60 °C. [AIBN] = 1.21 × 10^{-3} mol/L.

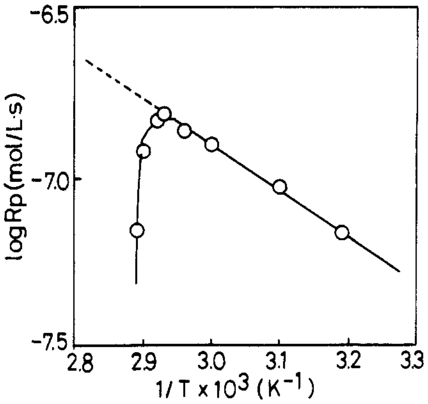


Figure 4. Plot of log R_p versus $1/T$ for the polymerization of BMI.

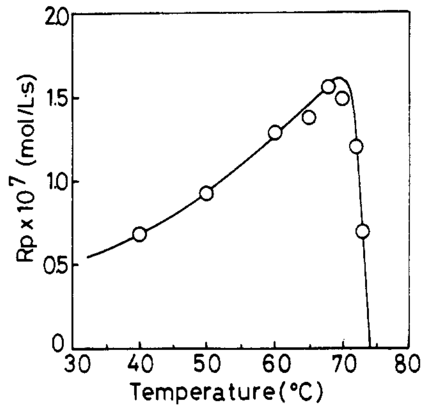


Figure 5. Plot of R_p versus temperature for the polymerization of BMI.

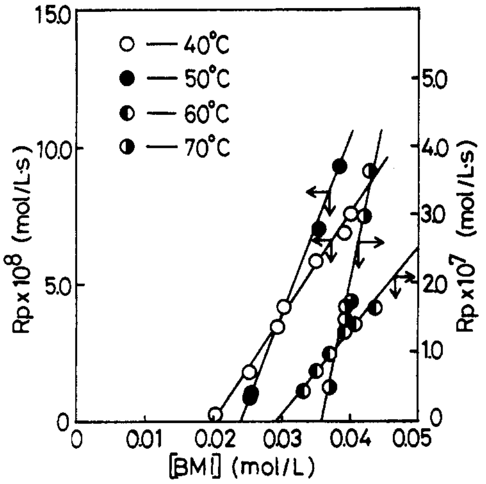


Figure 6. Plots of R_p versus [BMI] at various temperatures of 40 (○), 50 (●), 60 (◐), and 70 (◑) °C.

follows a square-root dependence on initiator concentration similar to a conventional radical polymerization. A log–log plot of R_p versus monomer concentration, [BMI], at 60 °C does not display a straight line as shown in Figure 3. In the monomer concentration range above 0.039 mol/L, the plot appears as a straight line with a slope of unity, while in the monomer concentration region below 0.038 mol/L, its slope deviates greatly, with the less the concentration, the steeper the slope. In the high monomer concentration region the polymerization rate shows a first-order dependence on monomer concentration as a conventional radical polymerization, whereas in the low monomer concentration it exhibits a much higher order dependence on monomer concentration. As shown in Figure 4, a plot, the so-called Arrhenius plot, of log R_p versus the reciprocal of the absolute polymerization temperature, $1/T$, with the monomer concentration of 0.0395 mol/L displays a straight line in the polymerization temperature range below 65 °C. The activation energy was estimated to be 23.2 kJ/mol. On the other hand, in the polymerization temperature range above 65 °C, it deviates greatly from the straight line, indicating significant decrease instead of increase in polymerization rate with polymerization temperature. The relationship of polymerization rate, R_p, versus polymerization temperature with monomer concentration of 0.0395 mol/L is shown in Figure 5. R_p increases with temperature in the temperature region below 65 °C, whereas it decreases sharply with polymerization temperature above 70 °C and its extrapolation to the rate of zero gives the polymerization temperature of about 74 °C, above which no polymerization takes place apparently. Therefore, it is obvious that both types of dependence of R_p on monomer concentration and on polymerization temperature seriously deviate from the corresponding ones for a conventional radical polymerization, suggesting a great contribution of depolymerization to the polymerization of BMI at high temperature and in low monomer concentration. The ceiling temperature, T_c, in the radical polymerization of BMI with a monomer concentration of 0.0395 mol/L is determined to be 74 °C as shown in Figure 5.

Rates of polymerization, R_p, at 40, 50, 60, and 70 °C are plotted against monomer concentration as shown in Figure 6 to give linear relationships, where extrapolation to the rate of zero allows one to obtain an equilibrium monomer concentration, $[BMI]_e$, at which the rate of polymerization is equal to that of depolymerization. The observed values of $[BMI]_e$ at respective polymeriza-

Table I
Equilibrium Monomer Concentration of BMI

temp, °C	$[BMI]_e$, 10^3 mol/L
40	19.9
50	24.1
60	29.2
70	36.6

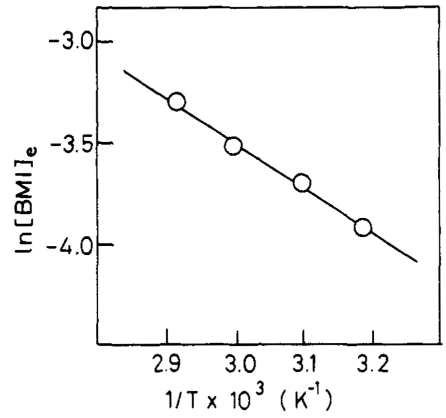


Figure 7. Plot of ln $[BMI]_e$ versus $1/T$ for the polymerization of BMI.

tion temperatures are summarized in Table I. The relationship between the log value of the equilibrium monomer concentration, $[BMI]_e$, and a reciprocal of the ceiling temperature, $1/T_c$, is shown in Figure 7 to be linear, as expressed by the equation[7]

$$\ln [BMI]_e = \Delta H/RT_c - \Delta S/R$$

where ΔH and ΔS are enthalpy and entropy changes for polymerization between the monomer and the polymer, respectively, and R is the gas constant. The values of enthalpy change and entropy change were determined to be −22.5 kJ/mol and −38.1 J/K·mol, respectively. Previously, we pointed out that ΔS values for homopolymerizable quinodimethane compounds are almost constant at about 40 J/K·mol, which is about one-third as large as the corresponding values for vinyl and related monomers.[5] BMI is considered to fall under the same class of homopolymerizable quinodimethane monomers.

The log–log plots of the so-called effective monomer concentration, $[BMI] - [BMI]_e$, versus R_p at various temperatures give straight lines with a slope of about 1.0 as shown in Figure 8. The rate of polymerization of BMI is expressed by the equation

$$R_p = k[AIBN]^{0.5}([BMI] - [BMI]_e)^{1.0}$$

where k is an apparent rate constant. It was concluded therefore that the polymerization of BMI can be well explained in terms of the radical polymerization under serious influence of depolymerization as one member of homopolymerizable quinodimethane compounds.[5]

Copolymerization of BMI with Styrene. The copolymerizations of BMI with styrene (St) were carried out at 60 °C with two monomer concentrations above and below the equilibrium monomer concentration of BMI ($[BMI]_e$ = 0.0292 mol/L at 60 °C). These results are summarized in Table II, and their composition diagrams are shown in Figure 9. The copolymers obtained were always composed of about 50 mol % of the BMI monomer unit regardless of monomer feed ratios and monomer concentration of BMI.

Figure 10 illustrates IR spectra of the BMI monomer and the copolymer of BMI with St of run no. 1. The BMI monomer shows absorptions at 1540 and 1460 cm^{-1}, which are assigned to exocyclic C=C and C=N stretching, respectively, but the copolymer does not exhibit these absorptions. Therefore, it is conceivable that BMI reacts at its exocyclic carbon and nitrogen sites.

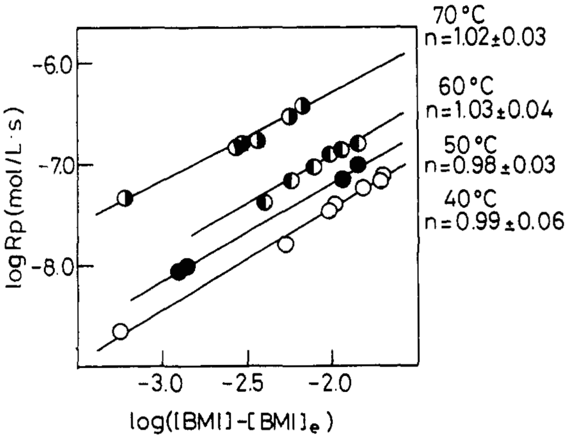


Figure 8. log–log plots of R_p versus $[BMI] - [BMI]_e$ at various temperatures of 40 (○), 50 (●), 60 (◐), and 70 (◑) °C. [AIBN] = 1.21×10^{-3} mol/L.

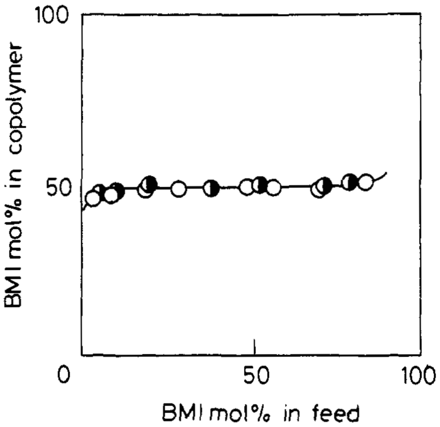


Figure 9. Composition diagrams for the copolymerization of BMI with St at 60 °C: (○) [BMI] = 0.0396 mol/L, (◑) [BMI] = 0.0198 mol/L.

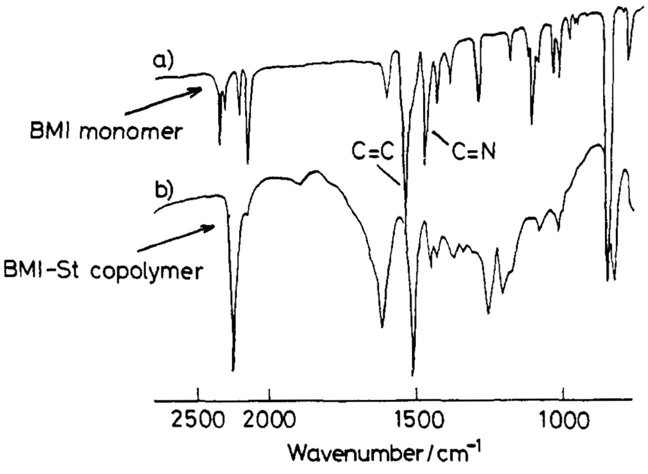


Figure 10. IR spectra of (a) BMI and (b) its copolymer with St.

The ^1H NMR spectrum of the copolymer of the run no. 1 is shown in Figure 11. The methine and methylene protons of the St monomer unit of the copolymer appear at the 5.0 and 3.7 ppm regions, respectively, indicating that they are much more subject to deshielding than the corresponding ones of polystyrene, generally appearing in the 1–2 ppm region.[8]

In the case of the alternating copolymer of 7,7,8,8-tet-

Table II
Copolymerization[a] of BMI with St

run	monomer feed BMI, mg	monomer feed St, mg	monomer feed BMI, mol %	solvent, mL	time, h	conv, %	copolymer compn anal., % H	copolymer compn anal., % C	copolymer compn anal., % N	copolymer compn BMI,[b] mol %	$\bar{M}_n$,[c] 10^4
					[BMI] = 39.6 mmol/L						
1	35.7	410.0	4.7	5.0	2.0	3.9	4.16	72.35	19.03	47.6	1.2
2	49.7	260.3	9.9	7.0	2.0	2.2	4.09	72.75	19.48	49.2	1.5
3	50.0	115.5	20.0	7.0	5.0	6.1	4.28	75.80	19.92	50.7	1.5
4	50.3	69.6	29.4	7.0	5.0	4.1	4.26	75.78	19.98	51.0	1.0
5	75.3	43.9	49.7	10.5	10.0	3.1	4.24	75.76	20.00	51.0	1.0
6	150.1	67.1	56.3	21.0	14.0	3.3	4.31	75.93	19.97	50.2	1.0
7	150.1	36.9	70.1	21.0	22.5	3.9	3.69	69.57	19.58	49.5	0.75
8	199.7	20.6	84.8	28.0	22.5	1.8	3.78	68.40	20.22	51.7	0.55
					[BMI] = 19.8 mmol/L						
9	35.8	393.5	5.0	10.0	5.0	2.9	4.26	74.70	19.37	48.8	1.5
10	49.6	266.3	9.7	14.0	14.5	11.2	4.08	73.59	19.59	49.6	1.5
11	49.8	118.5	19.5	14.0	15.0	7.6	3.98	75.92	20.11	50.5	1.3
12	50.2	65.1	30.8	14.0	14.5	5.3	4.33	75.99	19.68	49.9	1.0
13	75.5	39.7	52.3	21.0	22.0	6.7	3.18	76.08	19.66	49.8	0.8
14	150.3	35.2	71.1	42.0	31.0	3.8	3.62	68.50	19.53	49.3	0.45
15	200.0	29.2	79.8	56.0	31.0	1.5	4.13	74.88	20.13	51.4	0.35

[a] Initiator, AIBN, 1.0 mg. [b] Calcd from % N. [c] Determined by GPC; THF eluent.

Table III
Copolymerization of BMI with BCQ

run	monomer feed BMI, mg	monomer feed BCQ, mg	monomer feed BMI, mol %	solvent, mL	time, min	conv, %	copolymer compn anal., % H	copolymer compn anal., % C	copolymer compn anal., % N	copolymer compn BMI,[a] mol %	$\bar{M}_n$,[b] 10^5
1	24.7	113.1	30.0	3.5	18	21.4	5.81	64.92	8.49	4.8	1.8
2	35.6	105.3	39.9	5.0	12	8.5	5.92	66.35	8.95	8.4	1.0
3	49.9	99.9	49.5	7.0	160	33.9	5.86	65.47	9.23	10.5	0.5
4	50.4	96.1	50.7	7.0	32	25.1	5.93	66.49	9.25	10.8	1.0
5	50.1	71.4	57.9	7.0	40	9.2	5.89	65.24	9.67	13.9	0.76
6	75.3	76.2	66.0	10.5	77	8.7	5.92	67.87	10.19	17.6	0.77
7	75.4	63.3	70.0	10.5	160	16.5	5.67	66.54	10.45	20.6	0.22
8	99.6	49.8	79.7	14.0	105	3.9	5.43	65.63	11.56	26.9	0.28

[a] Calcd from % N. [b] Determined by GPC; THF eluent.

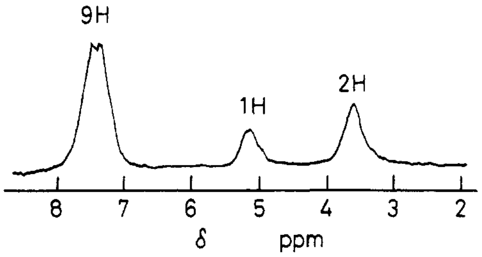
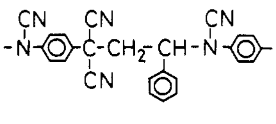


Figure 11. ^{1}H NMR spectrum of the copolymer of BMI with St.

racyanoquinodimethane (TCNQ) with St, the methine and methylene protons of the St unit were observed in the 3-4 ppm region.[9] The methine proton at 5.0 ppm (1 H) is obviously more subject to deshielding, so it is reasonable that its methine carbon combines directly with the nitrogen of the BMI unit. The methylene carbon at 3.7 ppm (2 H) combines with the dicyanomethylene of the BMI unit. It was concluded therefore that the St unit combines with the BMI unit in A form rather than



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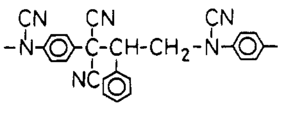

B

in B form and that BMI is attacked with the polymeric radical of the terminal St unit at the exocyclic nitrogen atom to yield the dicyanomethylene radical at the other end of the BMI unit, which then attacks the St monomer to give the benzyl-type radical of the St unit. The alternating copolymers obtained with the BMI monomer concentration under the equilibrium monomer concentration exhibit the same ^{1}H NMR spectrum as Figure 11. It is apparent that BMI copolymerizes with St always in alternating fashion regardless of BMI monomer concentrations even though BMI is homopolymerizable. Probably, it was thought that extremely great polar interaction between BMI and St plays a dominant role in determining the alternating fashion of copolymerization because BMI is almost as strongly electron accept-

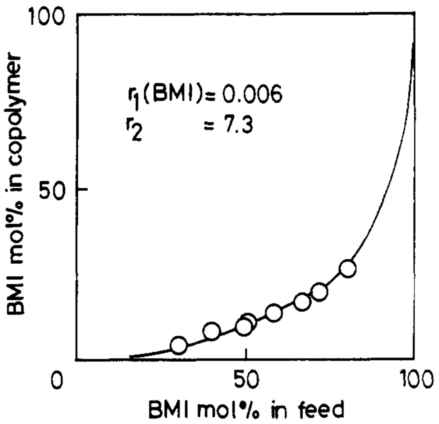

Figure 12. Composition diagram for the copolymerization of BMI with BCQ at 60 °C.

ing as TCNQ.

Copolymerization of BMI with BCQ. In order to estimate the monomer reactivity of BMI, copolymerization of BMI was carried out with a highly conjugative, electron-accepting monomer, 7,8-bis(butoxycarbonyl)-7,8-dicyanoquinodimethane (BCQ), in toluene at 60 °C. Because the homopolymerizations of BMI and BCQ are reluctantly influenced by depolymerization, their monomer concentrations were employed in copolymerization to be about 2 or 3 times as high as their equilibrium monomer concentrations. The results of the copolymerization are summarized in Table III, and their composition diagram is shown in Figure 12. The results were applicable without serious deviation to the intersection[10] and Kelen-Tüdös[11] methods to obtain monomer reactivity ratios, r_1(BMI) = 0.006 ± 0.005, r_2 = 7.3 ± 2.0 at 60 °C. The Alfrey-Price Q-e values of BMI were calculated by using the observed monomer reactivity ratios with Q and e values (9.3, +0.95) of BCQ[5] to be Q = 4.09 and e = +2.26. It is obvious that BMI is lower conjugatively (lower general reactivity) and much more electron accepting than BCQ.

Finally, it can be pointed out that N,7,7-tricyanobenzoquinone methide imine (BMI) is the most strongly electron-accepting monomer having homopolymerizability at the moment.

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Synthesis and Ring-Opening Polymerization of Novel Bicyclic Oxalactams. 2-Oxa-6-azabicyclo[2.2.2]octan-5-one

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ABSTRACT: A new bicyclic lactam, 2-oxa-6-azabicyclo[2.2.2]octan-5-one (2,6-BOL), was synthesized starting from acrolein and dimethyl malonate through a six-step reaction sequence. The anionic polymerization of 2,6-BOL using potassium pyrrolidonate and N-benzoyl-8-oxa-6-azabicyclo[3.2.1]octan-7-one as initiator and activator, respectively, at different temperatures ranging from 50 to 120 °C did not afford polyamide but a dimeric adduct (**9**) in low yield. Cationic polymerization of 2,6-BOL was initiated with trifluoromethanesulfonic acid and bis[(trifluoromethyl)sulfonyl]methane in dichloromethane and hexafluoroisopropyl alcohol at temperatures above −20 °C to yield powdery oligomers with molecular weights of several hundreds. Spectroscopic analysis disclosed that the oligomers were oligoethers containing 3,6-linked 2-piperidinone rings, which were produced by selective ring-opening reaction of 2,6-BOL at the C(1)-O(2) bond. The specific ring-opening polymerization behavior of 2,6-BOL is discussed in comparison with that of its structural isomer, 8-oxa-6-azabicyclo[3.2.1]octan-7-one (8,6-BOL).

Introduction

Ring-opening polymerization of heterobicyclic compounds containing two or more heteroatoms in their ring skeletons provides a convenient and effective approach to designing specialty polymers of well-defined ring structures in their repeating units. Thus, a wide variety of polyacetals, polyesters, and polyamides having oxacycles in their main chains have been prepared by ring-opening polymerization of bicyclic acetals, oxalactones, and oxalactams.[1-3] Especially, polymers possessing six-membered tetrahydropyran rings are of practical importance, because the presence of tetrahydropyran rings often imparts desirable physical properties to the polymers including crystallinity, thermal stability, appropriate hydrophilicity, and excellent mechanical properties such as tenacity and modulus.

Among bicyclic oxalactams, ring-opening polymerization of 8-oxa-6-azabicyclo[3.2.1]octan-7-one (hereafter referred to as 8,6-BOL) has been most extensively investigated. It is readily polymerized anionically at room temperature to give amphiphilic polyamide 1 consisting of cis-2,6-linked tetrahydropyran rings.[4,5] The membranes of 1 and its block copolymers are characterized by excellent permeability for water and permselectivity for alkali-metal ions as well as solutes of various sizes in aqueous

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