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Syntheses of ABA Triblock Copolymers Initiated with Polymeric Metalloester

Toshimitsu Suzuki,* Osamu Yamada, Yoshimasa Murakami,
Yoshinobu Takegami, and Yoshihisa Watanabe

Department of Hydrocarbon Chemistry, Faculty of Engineering,
Kyoto University, Kyoto 606, Japan. *Received October 7, 1981*

ABSTRACT: Anionic polymerization of methyl methacrylate (MMA) and *tert*-butyl methacrylate (BMA) was initiated with lithiated polyoxirane diisobutyrate (PEDB, M_n = 1000 or 2700) in tetrahydrofuran (THF) or toluene. The resulting block copolymers were characterized by ^{1}H and ^{13}C NMR spectroscopy, gel permeation chromatography (GPC), and solvent extractions. The copolymers prepared in THF show unimodal and relatively narrow molecular weight distributions. Methanolysis of the block copolymer (M_n = 8700, center block M_n = 1000; unimodal and relatively narrow molecular weight distribution) followed by GPC analysis proved that the copolymer was a symmetric triblock copolymer. The stereosequence distributions of the polymethacrylate part in the copolymer appeared rich in syndiotactic triad when THF was used as a solvent or PEDB-4000 (M_n = 2700) was used as an initiator in toluene. An isotactic block of PMMA was obtained when PEDB-1000 was used as an initiator in toluene.

Introduction

Recently, block copolymers containing hydrophobic and hydrophilic blocks have received much attention from the biomedical point of view. Polyoxirane, which is commonly named poly(ethylene glycol), is one of the common hydrophilic groups studied.

In our previous papers,[1,2] we studied the preparation of hydrophobic–hydrophilic–hydrophobic ABA-type triblock copolymer. Block copolymers were synthesized by the polymerization of methyl methacrylate (MMA) initiated with the disodium salt of polyoxirane (PEO) in the presence of a crown ether or a cryptate. However, a transesterification reaction between PEO and the methoxy group in MMA was accompanied by polymerization, resulting in a PEO grafted block copolymer. Subsequently, we developed a benzylamino derivative of PEO (PEO-N) as an alternative initiator system for the polymerization of MMA.[1,3] The initiation with disodium or dilithium amide of PEO-N resulted in a PMMA–PEO–PMMA triblock copolymer having a unimodal and relatively narrow molecular weight distribution, but it was very difficult to obtain diamine derivatives of PEO having higher molecular weights quantitatively.

Rathke et al. found that the α positions of acetic acid esters were easily, almost quantitatively lithiated by the use of lithium bis(tetramethylsilyl)amide or lithium dialkylamide;[4,5] a further advance was reported by Lochmann et al., who initiated polymerization of MMA with the growing-end-like anion obtained by α-lithiation of methyl isobutyrate using lithium diisopropylamide. The initiation system polymerized MMA in high yield without side reactions.[6]

In this paper, we describe the polymerization of MMA and *tert*-butyl methacrylate (BMA) using a lithiated PEO diisobutyrate as a new initiator, resulting in linear triblock copolymers having unimodal and narrow molecular weight distributions in high yield.

Experimental Section

Materials. Tetrahydrofuran (THF), toluene, and benzene were distilled twice over $LiAlH_4$ under a nitrogen atmosphere and stored over 4A molecular sieves. Diisopropylamine was distilled over CaH_2 just before use. *n*-Butyllithium was prepared from lithium (metal) and *n*-butyl bromide in hexane and stored under an argon atmosphere. Commercial MMA was purified by the usual method and distilled at reduced pressure.[7] BMA was synthesized from methacrylic acid and isobutene in the presence of concentrated sulfuric acid, purified by vacuum distillation[8] [59.5–59.9 °C (52 mmHg)]. Both monomers were stored under an argon atmosphere.

PEO Diisobutyrate. Five grams of commercial PEO-1000 (M_n = 980) or PEO-4000 (M_n = 2580) was placed into a 50-mL flask equipped with a three-way cock and was freeze-dried from benzene solution. Dry benzene (10 mL) and 1–2 mL of anhydrous pyridine were added in an argon atmosphere. Isobutyryl chloride, 5 times in excess of the PEO hydroxy end groups, was added dropwise to the solution, cooled by a water bath, with vigorous agitation. The reaction mixture was allowed to stand for a day and then transferred to a centrifugal tube and centrifuged to remove the precipitate of pyridine hydrochloride. Supernatant was poured into a large amount of petroleum ether–diethyl ether mixed solvent (2:1 v/v). PEO diisobutyrate (PEDB) was recovered as a white precipitate. Crude PEDB was dried under reduced pressure, purified by repeated centrifugations from benzene solution to remove the pyridine hydrochloride, and reprecipitated into petroleum ether–diethyl ether mixed solvent. From IR, ^{1}H NMR, and elemental analyses the following results are obtained: IR 1740 cm^{-1} (C=O); ^{1}H NMR δ 3.63 (s, 87 H for PEDB-1000, 238 H for PEDB-4000, $-(OCH_2CH_2)-_n$), 2.57 (m, 2 H, CH), 1.16 (d, 12 H, CH_3).

Anal. (PEDB-1000) Calcd for $C_{52}H_{102}O_{25}$: C, 55.4; H, 9.06. Found: C, 54.7; H, 9.09. (PEDB-4000) Calcd for $C_{126}H_{250}O_{62}$: C, 54.9; H, 9.08. Found: C, 55.5; H, 9.20.

The molecular weights measured by VPO (M_n = 1100 for

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Table I
Polymerization of Alkyl Methacrylates Initiated with Lithiated PEDB[a]

no.	monomer	initiator	M/I[b]	solvent	temp/ °C	time/ h	yield/ %	MW-(calcd)[c]/ 1000	M_n[d]/ 1000	M_w[d]/ 1000	M_w/M_n
1	MMA	1000	25	toluene	−25	1	94	6.1	12	57	4.7
2	MMA	4000	28	toluene	0	2	98	8.2	14	35	2.5
3	MMA	1000	30	THF	−10	1	91	7.1	8.7	14	1.6
4	MMA	4000	28	THF	0	2	96	8.2	14	21	1.5
5	MMA	1000	49	toluene	−20	0.1	96	11	18	32	1.8
6	MMA	4000	62	toluene	0	1	94	15	65	200	3.1
7	MMA	1000	61	THF	0	2	99	13	17	30	1.7
8	MMA	4000	57	THF	−5	2	97	14	9.5	17	1.8
9	MMA	4000	110	toluene	0	0.5	100	25	35	210	5.9
10	MMA	4000	104	THF	0	2	91	23	33	69	2.1
11	BMA	4000	43	toluene	0	3	100	15	46	63	1.4
12	BMA	4000	42	THF	0	2	100	15	33[e]	42	1.3
13	BMA	4000	95	toluene	0	1	100	30	62	93	1.5
14	BMA	4000	102	THF	0	4	100	32	69	113	1.6

[a] Initiator, 200 mg; solvent, 20–30 mL. [b] Monomer units/initiator ends. [c] Calculated from the value of M/I. [d] Calculated from GPC traces. [e] M_n measured by VPO is 16×10^3.

PEDB-1000, M_n = 2700 for PEDB-4000) were in good agreement with those calculated from the PEO used (M_n = 1120 and 2720).

Lithium Diisopropylamide. Under an argon atmosphere, diisopropylamine (1.6 mmol) was added to 2.0 mL of benzene, which was trap-to-trap distilled from a benzene solution of oligostyryllithium just before use. To this solution an equivalent amount of *n*-butyllithium (1.12 mol/L) was added at around 15 °C. The absence of the absorption at 3320 cm^{-1} of the N-H stretching vibration in the infrared spectrum of the reaction mixture shows completion of N-lithiation.

Initiator. PEDB (200 mg) was placed in a two-necked flask and was freeze-dried from benzene solution. Then 20–30 mL of solvent was vacuum distilled into the flask. THF was distilled from material containing sodium benzophenone and toluene from oligostyryllithium. The PEDB solution was cooled to 0–18 °C, and lithium diisopropylamide, equivalent to the ester group of PEDB, was added with stirring and then allowed to stand. Portions of the reaction mixture were removed at intervals and analyzed by infrared spectroscopy. A red shift of the characteristic absorption from 1740 to 1670 cm^{-1} attributed to the C=O stretching of the ester group was observed as shown in Figure 1.[9] The lithiation reaction of PEDB in toluene proceeded to about 70% after 30 min and almost to completion after 1 h at 0 °C. In the case of the diisobutyric ester of PEO-4000, it is difficult, due to the low solubility and the low concentration of terminal groups, to follow the change in the IR spectrum during the lithiation reaction. In this case, we employed a reaction time of 1 h at 15 °C.

Polymerization. The polymerization reaction was initiated by the addition of a certain amount of MMA or BMA monomer at the prescribed temperature. After a given time, the polymerization was stopped by adding a small amount of 2-propanol. The reaction mixture was poured into a large amount of hexane. The polymer was filtered off, washed with hexane, and dried under vacuum at room temperature.

Characterization of Copolymers. Gel permeation chromatograms (GPC) were recorded on a Waters ALC/GPC 244 equipped with four μ-Styragel columns ($10^5 + 10^4 + 10^3 + 500$ Å), with THF as eluent (1.5 mL/min at ambient temperature). Standard polystyrenes were used for calibration. The weight-average molecular weight (M_w) and number-average molecular weight (M_n) of the polymers were estimated from their GPC traces. The true molecular weights of the polymers may somewhat deviate from those of standard polystyrenes due to the differences in their hydrodynamic volumes.

^{13}C NMR spectra were recorded at 25.0 MHz and ^1H NMR spectra at 100.0 MHz in the pulse Fourier transformation mode on a JEOL FX-100 spectrometer, using 10–20% (w/v) $CDCl_3$ solutions of the polymers at ambient temperature or 50 °C.

Results and Discussion

Polymerization of MMA and BMA. Polymerization of methacrylic acid esters initiated with dilithio-PEDB was complete within a few minutes. The rate of polymerization in toluene was apparently faster than that in THF, especially in the case of MMA. Since nearly 100% yield was obtained in all cases, polymerization times in this series of experiments are considered to have no significant meaning. The results are summarized in Table I. In this table, M/I is the ratio of monomer units to initiator terminal groups, and calculated molecular weights (MW(calcd)) were simply obtained from the value of M/I.

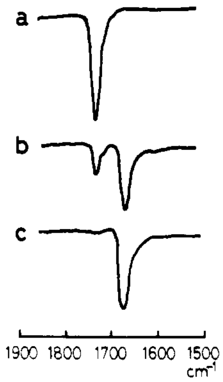

Figure 1. Infrared spectra of lithiated PEDB: (a) before metalation; (b) 30 min after metalation; (c) 1 h after metalation.

Characterization of Block Copolymers. In the case of the polymerization of MMA, the resulting polymer recovered from hexane, which is a poor solvent for both PMMA and PEDB, may contain unreacted PEDB or occasionally homo-PMMA. A small amount of unreacted PEDB was detected by GPC when the value of M/I increased (no. 9 and 10). It is impossible to ascertain the formation of block copolymer only by spectroscopic methods such as IR and NMR. To remove the unreacted initiator fragment, fractionation using methanol, which is a good solvent for PEO, was carried out for the copolymer of PMMA and PEO. Polymer no. 8 (M/I = 57), having a relatively low molecular weight, dissolved in methanol completely, and furthermore, it was highly dispersed in water to give a milky white emulsion in water. This phenomenon is quite different from the behavior of the copolymer previously obtained with the disodium salt of PEO (M/I = 50), which could be fractionated from acetone solution of the copolymers with methanol.[1] The polymers having relatively high molecular weights, such as no. 10, were fractionated with methanol. In the ^1H NMR spectra of methanol-insoluble fractions, an absorption at δ 3.62,

Table II
Fractionation of PEO-*b*-PMMA and PEO-*b*-PBMA

no.	monomer	yield of fraction/%	monomer units[c]/ PEO chain	$M_n{}^d$/1000
4	MMA	42[a]	106	23
6	MMA	78[a]	365	65
10	MMA	90[a]	217	42
13	BMA	58[b]	436	61
14	BMA	32[b]	803	96

[a] Methanol-insoluble fraction. [b] Hexane-soluble fraction. [c] Obtained from ^{1}H NMR spectra. [d] Calculated from GPC traces.

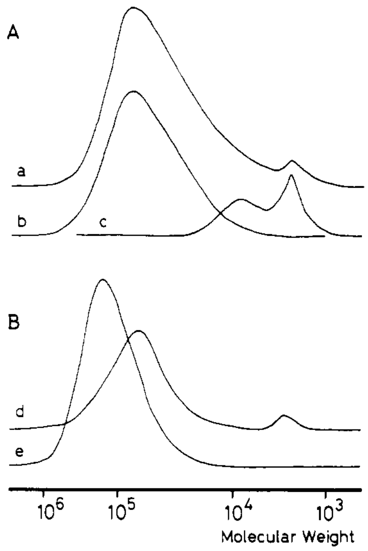

Figure 2. Fractionation of copolymers. (A) PEO-*b*-PMMA (no. 10): (a) whole polymer; (b) methanol-insoluble fraction; (c) methanol-soluble fraction. (B) PEO-*b*-PBMA (no. 14): (d) hexane-insoluble fraction; (e) hexane-soluble fraction.

attributed to the methylene protons of PEO, was observed in addition to that of the methoxy protons of PMMA at δ 3.59. In this way, it is demonstrated that these polymers are block copolymers formed by addition of the MMA monomers to the PEDB dianions.

Copolymers containing BMA were dissolved in methanol or 2-propanol. When a solution of the polymer was poured into a large amount of hexane, unreacted PEDB and a polymer containing large quantities of PEO were precipitated. On the other hand, high molecular weight PBMA was recovered by evaporating the solvent. ^{1}H NMR spectra of hexane-soluble fractions clearly showed a sharp absorption of the methylene protons of PEO at δ 3.62, indicating the formation of block copolymers of PEO and PBMA. The results of fractionation of copolymers are summarized in Table II, and GPC traces of the fractionated polymers are shown in Figure 2. In the case of copolymer no. 10, which is recovered almost completely as a methanol-insoluble part, the number of MMA units per PEO chain, 217, obtained from the relative intensities of the above resonances, is in good agreement with the theoretical value, 208 (twice the M/I value). In the case of fractionated PEO-*b*-PMMA, the M_n obtained from the GPC trace is larger than that calculated from the ^{1}H NMR spectrum. On the other hand, the M_n obtained from the GPC trace of fractionated PEO-*b*-PBMA containing a large amount of PBMA agrees well with the molecular weight calculated from the ^{1}H NMR spectrum. This is different from the results in which M_n obtained from GPC appeared twice as large as that expected from M/I. These results indicate that the hydrodynamic volume of the block copolymer varies widely according to the size of the ester groups or the composition of the copolymers.

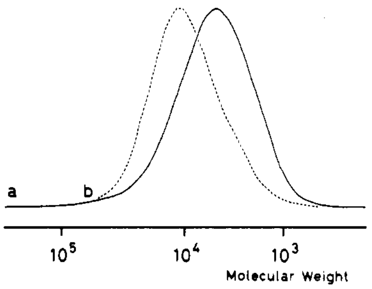

Figure 3. Gel permeation chromatogram of product obtained by methanolysis of PEO-*b*-PMMA: (a) product of methanolysis; (b) original polymer (no. 3).

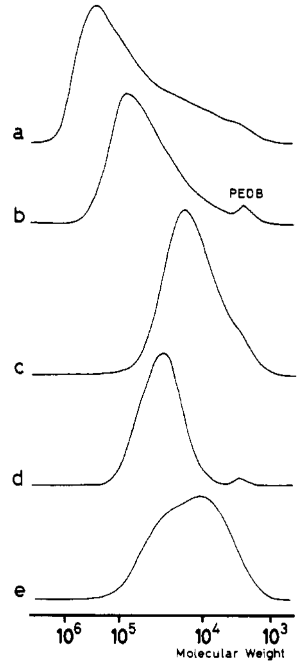

Figure 4. Gel permeation chromatograms of PEO-*b*-PMMA and PEO-*b*-PBMA: (a) no. 9; (b) no. 10; (c) no. 8; (d) no. 12; (e) PEO-*b*-PMMA initiated with the disodium salt of PEO.

Although copolymers prepared in this manner are identified as block copolymers, it is difficult to know whether they are triblock copolymers or diblock copolymers. As the block copolymer thus obtained contains aliphatic ester linkages in the main chain, we expect to obtain each component of the block copolymer by hydrolysis. If we record the gel permeation chromatogram before and after hydrolysis, we will obtain information about the chain length of the PMMA block of the copolymer.[10] Methanolysis of the ester linkages in the main chain of block copolymer no. 3 (M_n = 8700) was carried out in the presence of sodium methoxide in THF at room temperature. In Figure 3, GPC traces of the original copolymer (dotted line) and hydrolyzed polymers (full line) are shown. The molecular weight of the product (M_n =

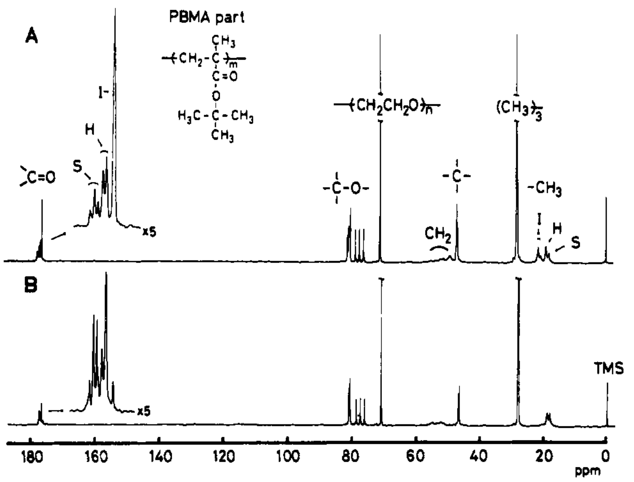

Figure 5. ^{13}C NMR spectra of PEO-*b*-PBMA: (A) no. 11; (B) no. 12.

4200) is about half the original polymer's (M_n = 8700) and is in good agreement with the theoretical molecular weight of the A block of the symmetric ABA triblock copolymer (M_n = 3900). This clearly indicates that the original copolymer consists mostly of symmetric triblock copolymer.

Relation between M/I and Molecular Weight Distributions of Copolymers. Figure 4 shows GPC traces of typical copolymers obtained, together with the copolymer prepared by the previous method.[1] In general, copolymers prepared in THF at lower M/I ratios showed narrower and symmetric molecular weight distributions (no. 8). This type of copolymer, as the molecular weight observed was in fair agreement with that calculated and the unreacted initiator fragment was not observed, can be considered to contain a large portion of triblock copolymer. When the M/I ratio increased to around 100 or larger, the viscosity of the polymerization system increased instantaneously upon addition of the monomer. Such a tendency is more accelerated when toluene is the polymerization solvent. GPC traces of the copolymer obtained in such conditions are skewed and the peak molecular weight is shifted to a higher molecular weight region than expected as shown in no. 9 and 10 in Figure 3. Although the copolymer obtained in THF under the condition of M/I = 104 (no. 10) showed a relatively narrow molecular weight distribution, a certain amount of unreacted PEDB (20% of the whole initiator) was observed in the GPC trace. Such copolymers seem to contain not only symmetric triblock copolymers but also a certain amount of diblock or dissymmetric triblock copolymers.

In the polymerization of BMA, the copolymer was recovered in a high yield and had a narrow and symmetric molecular weight distriution both in THF and in toluene. This is due partly to the lower viscosity of the reaction system in the polymerization of BMA than that in the case of MMA. The molecular weight of the resulting polymer (from GPC) is about twice as large as that expected, and when the value of M/I increased to 100, the molecular weight distribution was broadened slightly. However, the molecular weight of polymer no. 12 obtained from VPO measurement agreed well with that expected. Thus the differences in M_n and MW(calcd) in Table I could be attributed to the differences in the molecular size of polystyrene and the block copolymer in THF. Copolymer containing PBMA, prepared under conditions of lower M/I, contains a small amount of unreacted PEDB (3% for no. 12) and has a narrow symmetric molecular weight distribution. Although hydrolysis of the block copolymer was not carried out, the copolymer seems to be a triblock copolymer.

Table III
Stereosequence Distributions of the Poly(methacrylic acid ester) Part in the Block Copolymers

no.	monomer	initiator	M/I	solvent	triad tacticity[a]/% I	H	S
5	MMA	1000	49	toluene	64	24	12
6	MMA	4000	62	toluene	9	35	56
7	MMA	1000	61	THF	4	38	58
8	MMA	4000	57	THF	0	40	60
11	BMA	4000	43	toluene	39	40	21
12	BMA	4000	42	THF	7	47	46

[a] I = isotactic triad, H = heterotactic triad, and S = syndiotactic triad.

Table IV
Stereosequence Distributions of the PMMA Part in the Fractionated Copolymers

		triad tacticity (%) of methanol-soluble part			triad tacticity (%) of methanol-insoluble part		
no.	solvent	I	H	S	I	H	S
7	THF	4	38	58	4	38	58
2	toluene	18	40	42	8	33	59
9	toluene	29	39	32	11	37	52

Stereosequence Distributions of Poly(methacrylic acid ester) Blocks in the Copolymers. The triad tacticity of the PMMA part in the copolymer was calculated from the splitting of the resonance of the α-methyl protons.[11] The triad tacticity of PBMA cannot be obtained from the ^1H NMR spectra due to overlapping of the absorption of α-methyl protons with the strong absorption of the *tert*-butyl group. ^{13}C NMR spectra were employed as shown in Figure 5. Triad tacticity was obtained from the partially resolved pentad splitting of carbonyl carbon resonances according to the assignment made for PMMA by Inoue et al.[12] Stereosequence distributions of methacrylic acid ester blocks in the copolymers are summarized in Table III. The fraction of isotactic triad is high when toluene is used as a solvent. On the other hand, the fraction of syndiotactic triad increases when THF is used. However, the fraction of isotactic triad remarkably decreases even in toluene if PEDB-4000 is used as an initiator. It can be explained that PEO units of the initiator in PEDB-4000 contribute to the solvation of countercations inter- or intramolecularly and weaken the interaction between growing chain ends and lithium countercations. The chain length of PEO-1000 is not long enough to solvate the lithium cation compared with PEDB-4000. Triad tacticities of the PMMA part of the block copolymers fractionated by methanol are shown in Table IV. As listed, the portion of isotactic triad in the lower molecular weight fraction is larger than that in higher ones. It is indicated that the interaction between the growing chain end and the countercation is not so weak in the initial stage of polymerization. When the PMMA chain grows longer, less hindered interaction between the PEO chain and countercation occurred to give syndiotactic-rich PMMA. This result seems to indicate that the interaction between the PEO chain and countercation on the living chain end may partly associate in the intramolecular process.

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Perfluoroalkylene-Linked Polyquinolines and Related Model Compounds

Francesco A. Bottino, Antonino Mamo, and Antonino Recca*

Faculty of Engineering, University of Catania, 95125 Catania, Italy

John P. Droske and John K. Stille*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

Received August 10, 1981

ABSTRACT: The synthesis of perfluoroalkylene-linked polyquinolines and related model compounds and the effect of the perfluoroalkylene group on the physical and chemical characteristics of these polymers are described. While the glass transition temperatures of all of the perfluoroalkylene polyquinolines were significantly lower than those of the all-aromatic polyquinolines, the thermal stability was lower only with a large incorporation of perfluoroalkylene groups; i.e., 5% perfluoroalkylene copolymers showed thermal stabilities equal to those of the all-aromatic polyquinolines. The solution viscosity decreased with an increasing incorporation of perfluoroalkylene units. Thus, measurement of the dynamic mechanical properties was only possible with 5% copolymers which had sufficiently high solution viscosities to permit casting good films.

Introduction

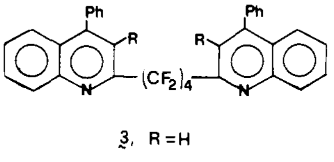
The Friedlander reaction has been used extensively to afford high molecular weight polyquinolines.[1-4] The polyquinolines show excellent thermal stability,[1-5] but their processability is often quite limited because of the high T_g's and, in some cases, the low solubility exhibited by these polymers. In an effort to increase the processability of these polyquinolines, the incorporation of flexible fluoromethylene groups into the polymer chain has been investigated and is reported herein. Fluoromethylene incorporation into the chain is appropriate for this purpose because it lowers T_g and maintains chemical inertness as well as thermal, thermooxidative, and radiative stability.[6-13]

Discussion

Syntheses. The synthesis of 3,3,4,4,5,5,6,6-octafluoro-2,7-octanedione (**1**) and 1,8-diphenyl-3,3,4,4,5,5,6,6-octafluoro-2,7-octanedione (**2**) was accomplished by the Grignard reaction of octafluoroadipic acid with methyl- and benzylmagnesium halides (eq 1).

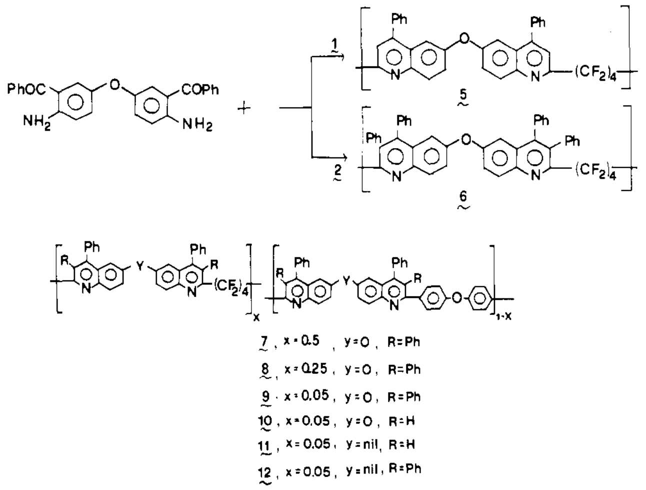
$$\mathrm{HOOC(CF_2)_4COOH + RMgX} \rightarrow \mathrm{RCH_2C(O)(CF_2)_4C(O)CH_2R} \quad (1)$$
$$\mathbf{1},\ \mathrm{R = H}$$
$$\mathbf{2},\ \mathrm{R = C_6H_5}$$

The bisquinolines **3** and **4** were prepared by the reaction of 3,3,4,4,5,5,6,6-octafluoro-2,7-octanedione (**1**) or 1,8-diphenyl-3,3,4,4,5,5,6,6-octafluoro-2,7-octanedione (**2**) with 2-aminobenzophenone in a chloroform–di-*m*-cresyl phosphate medium.[4] The presence of the parent ions (*m/e* 608 and 760 for **3** and **4**, respectively) in the mass spectrum of both materials was an indication of their stability.



3, R=H
4, R=Ph

Scheme I



All polymerizations were conducted in *m*-cresol–di-*m*-cresyl phosphate medium.[4] Polymers **5** and **6** were prepared by the reaction of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether with monomers **1** and **2**, respectively, while copolymers **7–9** were obtained from 4,4′-diamino-3,3′-dibenzoyldiphenyl ether with monomer **2** and 4,4′-diphenacetyldiphenyl ether in the appropriate balance (Scheme I). The polymerization of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether with monomer **1** (5%) and 4,4′-diacetyldiphenyl ether (95%) afforded copolymer **10**, and copolymers **11** and **12** were prepared from 3,3′-dibenzoylbenzidine[3] with 4,4′-diacetyl- or -diphenacetyldiphenyl ether and monomers **1** and **2**, respectively, in the appropriate balance.

Phase Transition Temperatures, Thermal Stabilities, and Dynamic Mechanical Properties. Pressed powder samples of the perfluoroalkylene-linked poly-

0024-9297/82/2215-0227$01.25/0