

Preparation and Characterization of Polycarbonates from 2,4,8,10-Tetraoxaspiro[5,5]undecane-3-one (DOXTC)–Trimethylenecarbonate (TMC) Ring-Opening Polymerizations

XIANHAI CHEN, STEPHEN P. MCCARTHY, RICHARD A. GROSS

NSF Biodegradable Polymer Research Center, University of Massachusetts Lowell, One University Ave., Lowell, Massachusetts 01854

Received 11 December 1996; accepted 31 May 1997

ABSTRACT: The new cyclic carbonate monomer 2,4,8,10-tetraoxaspiro[5,5]undecane-3-one (DOXTC) was prepared in > 80% yield by the reaction of 1,3-dioxane-5,5-dimethanol with ethyl chloroformate in tetrahydrofuran (THF). DOXTC homopolymerization and copolymerizations with trimethylene carbonate (TMC) were carried out using aluminoxanes (methyl and isobutyl) as catalysts. The copolymer yields normally exceeded 90%. Carbon-13 (^{13}C) nuclear magnetic resonance (NMR) at 62.5 MHz resolved copolymer dyad sequences. Comparison of the fraction of dyad sequences determined by ^{13}C -NMR and calculated assuming a Bernoullian distribution showed that propagation statistics were approximately random for copolymerizations carried out at both 90 and 140°C. Studies by differential scanning calorimetry (DSC) showed that the DOXTC homopolymer, as well as the copolymers with high DOXTC content (F_{DOXTC} to $F_{\text{TMC}} \geq 7 : 3$), were semicrystalline. The DOXTC homopolymer had a peak melting temperature of 202°C, enthalpy of fusion of 75 J/g, and a glass transition temperature of 36°C. For copolymers with F_{DOXTC} to $F_{\text{TMC}} \geq 9/1$, crystallization exotherms were observed both during the second heating, as well as cooling (10°C/min) DSC scans. The relationship between the copolymer glass transition and composition was in agreement with that predicted by the Fox equation. Comparison of the wide-angle X-ray scattering (WAXS) patterns of the DOXTC homopolymer with F_{DOXTC} to F_{TMC} of 7 : 3 and 9 : 1 showed that the former sample had more pronounced and better resolved crystalline reflections. These results suggest that the DOXTC homopolymer has well-ordered crystalline domains and high sample crystallinity. By increasing the molar content of 1,3-dioxane side groups in DOXTC–TMC copolymers from 0 to 50%, the water uptake by the corresponding films was increased from 5.1 to 19% (w/w). © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 547–557, 1998

Key words: cyclic aliphatic carbonate; monomer synthesis; organometallic catalysts; ring-opening copolymerization; crystallinity

INTRODUCTION

Stimulated by the need for bioresorbable medical materials with a wide range of physical properties

and degradation rates, there has been considerable interest in exploring aliphatic polycarbonates prepared by the ring-opening polymerization (ROP) of cyclic carbonate monomers.^{1–7} Efforts have thus far focused on polymerizations of five- and six-membered ring aliphatic cyclic carbonates. Irrespective of the catalyst used, polymerizations of the five-membered ring monomers ethylene car-

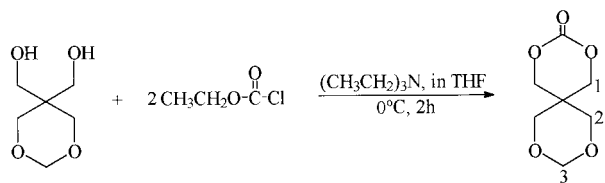
Correspondence to: R. A. Gross.

Journal of Applied Polymer Science, Vol. 67, 547–557 (1998)
© 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/030547-11

bonate⁸ and 1,2-propylene carbonate⁹ were accompanied by loss of CO₂ (decarboxylation), resulting in ether linkages along the chain. The molar fraction of ethylene carbonate or 1,2-propylene carbonate repeat units was not higher than 0.5.⁸ In contrast, copolymerization of CO₂ with either ethylene oxide or propylene oxide resulted in polycarbonates having carbonate molar fractions approaching 1.0 and/or high molecular weights.^{10–12} The anionic ROP of six-membered cyclic carbonates gives copolymers comprised of repeat units, which are identical to those that would be derived from the perfectly alternating copolymerization of the corresponding cyclic ether and CO₂.¹³ For example, no decarboxylation was observed for the anionic polymerization of 2,2-dimethyltrimethylene carbonate (DTC).¹⁴ In contrast, the cationic polymerization of both five- and six-membered ring cyclic carbonates has, in all cases, resulted in substantial decarboxylation.¹⁵

To date, the majority of publications on the ROP of 2,2-disubstituted six-membered cyclic carbonates used the anionic initiator *sec*-BuLi. The polymerizability of these monomers decreased as the size of the substituents at the two-position increased.¹⁶ For example, comparison of the ROP of 2-methyl-2-phenyl trimethylene carbonate¹⁷ and DTC¹⁴ using *sec*-BuLi as initiator and similar reaction conditions showed that polymerization of the former monomer resulted in lower polymer yields (<50% versus > 70%) and molecular weights ($M_n < 8000$ versus > 30,000 g/mol). Attempts to homopolymerize 2,2-diphenyl trimethylene carbonate have been unsuccessful.¹⁷

Thus far, there have only been a few reports on the use of Zn-, Al-, and Sn-based organometallic catalysts for cyclic carbonate ROPs. Examples include (1) work by Kuhling et al.,¹⁸ where ZnEt₂, Al(O-*sec*-Bu)₃, and Bu₂Sn(OMe)₂ were used to catalyze DTC ROP; and (2) trimethylene carbonate (TMC) polymerizations by Kricheldorf and Weegen-Schulz,¹⁹ as well as Albertsson and Sjöling²⁰ by Bu_nSnCl_{4-n} ($n = 1$ to 3), Bu₂SnO, Sn(Oct)₂, and Al(O-*iso*-Pr)₃ catalysis. The work of Albertsson and Sjöling²⁰ showed that Al(O-*iso*-Pr)₃-catalyzed TMC polymerization at 80°C for 4 h resulted in poly(trimethylene carbonate) (PTMC) with an M_n of 56,000 g/mol ($M_w/M_n = 1.8$). Also, Schmidt et al.²¹ reported that DTC polymerization for 36 h by Al(O-*sec*-Bu)₃ catalysis at 90°C resulted in PDTC with an M_n of 21,200 g/mol (45% yield). The polymerizations catalyzed by organometallic compounds described in the literature^{18–20} gave polycarbonates without decarboxylation. It is noteworthy with respect to this



Scheme 1

article to consider the following: (1) these catalyst systems have not been investigated for polymerizations of 2,2-disubstituted cyclic carbonates having substituents that are larger than methyl groups; and (2) the family of aluminoxanes, which have proven to be efficient catalysts for lactone ROPs, have not as yet been evaluated for carbonate ROPs.

In addition to effecting monomer polymerizability, the substituents at the two-position of cyclic trimethylene carbonates can be used to tailor the thermal and physicomechanical properties of the resulting polymeric materials. Results on the relationship between the two-position substituent(s) and the glass transition temperature (T_g), peak melting temperature (T_m), and the enthalpy of fusion (ΔH_f) have been reported for a few different polycarbonates. For example, while PTMC has a $T_g = -16^\circ\text{C}$ and is essentially amorphous (see below and Zhu et al.,²²), poly(2,2-dimethyltrimethylene carbonate) (PDTC) has a relatively higher T_g (27°C) and is semicrystalline ($T_m = 108^\circ\text{C}$; $\Delta H_f = 20$ J/g).¹⁴ Interestingly, poly(2-ethyl-2-hydroxymethyl trimethylenecarbonate) had similar thermal properties as PDTC ($T_g = 27^\circ\text{C}$; $T_m = 117^\circ\text{C}$).²³ The monomer 5,5-(Bicyclo[2,2,1]hept-2-en-5,5-ylidene)-1,3-dioxan-3-one (NC) has a relatively larger rigid substituent than the monomers described above, which resulted in a polymer with T_g and T_m transitions at 60 and 117°C, respectively.¹⁶ Poly(2-allyloxy-methyl-2-ethyl-1,3-dioxan-2-one) (PAEMC), which has flexible and relatively larger 2,2-substituents than PDTC, had a T_g of -30°C .²⁴

Based on our interest in biodegradable and bioerodable polymers of environmental and medical importance, we have initiated a program to explore the polymerizability of various 2,2-disubstituted trimethylene carbonates to gain insight into how the structure of the 2,2-substituents affects the physicomechanical and biological properties of the corresponding polymeric materials. In this article, we describe the preparation of the following new six-membered cyclic carbonate: 2,4,8,10-tetraoxaspiro[5,5]undecane-3-one (DOXTC) [see Scheme (1)]. The spiroconnected 1,3-dioxane side groups of poly-

merized DOXTC were of interest relative to studies with DTC since they are relatively larger, may increase chain rigidity due to their cyclic structure, and are expected to increase chain hydrophilicity. Copolymerizations of DOXTC with TMC and DOXTC homopolymerization were studied using aluminoxanes as catalysts. The influence of DOXTC 1,3-dioxane side groups on copolymer thermal properties was investigated. Copolymer microstructure as a function of the catalyst used was studied by ^{13}C nuclear magnetic resonance (NMR). Investigations were also carried out to establish relationships between copolymer composition and polymer solubility, crystallinity, and water absorption.

EXPERIMENTAL

Materials

Methylaluminumoxane (MAO; 2.03M in heptane) and isobutylaluminumoxane (IBAO; 0.95M in heptane) were from Akzo Chemical Inc. (IL, USA) and used as received. 1,3-Dioxane-5,5-dimethanol was purchased from Aldrich (WI, USA) and used as received. All liquid reagents were transferred by syringe under a dry argon atmosphere.

Synthesis of Monomers

2,4,8,10-tetraoxaspiro [5,5] undecane-3-one (DOXTC) was synthesized by the method reported by Ariga et al.,¹⁵ except that the reaction was conducted at 0°C instead of room temperature. The crude product was washed with ether and recrystallized from dry tetrahydrofuran (THF) (0°C) to give white needle crystals (>80% yield). Analysis of the product showed the following: mpt, 126.5–127.5°C; $^1\text{H-NMR}$ (chloroform-*d*), 4.86 ppm (H_3 , 2H, s), 4.41 ppm (H_1 , 4H, s), and 3.91 ppm (H_2 , 4H, s); and Fourier transform infrared (FTIR) spectrum (KBr pellet), 2865, 1729, 1465, 1191, 1171, and 1120 cm^{-1} . Trimethylenecarbonate (TMC) was prepared and purified following a method in the literature.¹⁵ The $^1\text{H-NMR}$ and FTIR spectra of TMC were identical to those previously given in the literature.²⁰

Polymerizations

The following is the general procedure used for DOXTC homopolymerization and DOXTC-TMC copolymerizations. Additional information on polymerization conditions, catalyst concentrations, comonomer feed ratios, and monomer-to-catalyst

ratios are given in Table I. The polymerization ampules (10 mL) were treated with trimethylsilyl chloride, washed with three 5 mL portions of methanol, dried at 100°C in an oven, flame-dried, and purged with dried argon. DOXTC, TMC (total 10 mmol), and the catalyst solution (see Table I) were transferred into the ampule using a glove box to maintain an inert nitrogen atmosphere. The ampule was degassed by several vacuum-purge cycles, sealed under argon, and placed in an oil bath maintained at 90 or 140°C for a predetermined reaction time. At the end of the reaction period, the contents of the ampule were dissolved in methylene chloride (10 mL), the methylene chloride solution was added to methanol (100 mL) to precipitate the polymer, the precipitate was washed with several portions of methanol, and then the volatiles were removed in a vacuum oven (<3 mmHg, 40°C, 24 h). Methylene chloride insoluble products, which contained > 50 mol % DOXTC, were ground into a fine powder and Soxhlet-extracted with methanol for 24 h to remove catalyst residue and unreacted monomer.

Instrumental Methods

Fourier Transform Infrared Spectroscopy

A P-E 1720 FTIR spectrometer was used to record IR spectra of monomers and polymers. KBr pellets were prepared, and the data was accumulated as follows: 16 scans; resolution 2 cm^{-1} , 4000 to 400 cm^{-1} .

Nuclear Magnetic Resonance

Proton (^1H) NMR spectra were recorded on a Bruker ARX-250 spectrometer at 250 MHz. $^1\text{H-NMR}$ chemical shifts in parts per million (ppm) were reported downfield from 0.00 ppm using tetramethylsilane (TMS) as an internal reference. The concentration used was 4% w/v in chloroform-*d*. The instrumental parameters were as follows: 300 K temperature; 7.80 μs (30°) pulse width; 32 K data points; 3.18 s acquisition time; 1 s relaxation delay; and 32 transients. The abbreviations for singlet and multiplet signals were *s* and *m*, respectively. Carbon-13 (^{13}C) spectra were recorded at 62.9 MHz on a Bruker ARX-250 spectrometer in chloroform-*d* solutions using CDCl_3 as the internal reference at 77.00 ppm. Polymer spectral acquisitions were conducted as 20% w/v chloroform-*d* solutions using the following parameters: 300 K temperature; 30° pulse width; 64 K data points; 1.638 s acquisition time; 1 s delay time; 10,000 to 15,000 transients.

Table I Polycarbonate Yields and Molecular Weights for Copolymerization of 2,4,8,10-tetraoxaspiro[5,5]undecane-3-one (DOXTC) with Trimethylenecarbonate (TMC) Using Aluminoxanes as Catalysts^a

Entry No.	Catalyst ^b	f_{DOXTC} to f_{TMC} (mol : mol)	t (°C)	Time (h)	Yield (%) ^d	M_n ^e	M_w/M_n ^e
1	MAO	0 : 1	90	2	96	80,500	1.9
2	MAO	1 : 9	90	2	98	81,700	3.1
3	MAO	3 : 7	90	2	100	39,800	6.2
4	MAO	1 : 1	90	2	93	8,819	3.2
5	MAO	1 : 1	140	0.5	100	39,400	4.3
6	IBAO	1 : 1	140	0.5	99	47,200	2.9
7	IBAO	7 : 3	140	0.5	97	nd ^f	nd
8	IBAO	9 : 1	140	0.5	92	nd	nd
9	IBAO	1 : 0	140	0.5	99	nd	nd

^a Reactions were carried out in bulk, $[M]_{\text{total}}/[A1] = 200$. For entries 1–6, analysis of products by ¹H-NMR showed that the monomer feed and copolymer composition (F_{DOXTC} to F_{TMC}) were identical.

^b See the Experimental Section for additional information.

^c Monomer feed molar ratio.

^d The percentage of yield was $100 \times \text{wt of purified polymer/wt of charged monomer}$.

^e Measured by GPC.

^f Poor product solubility did not permit analysis of molecular weight (nd = no data).

Molecular Weight Measurements

All molecular weights were determined by gel permeation chromatography (GPC) utilizing a Waters Model 510 pump, Model 410 differential refractometer, Waters 486 tunable absorbance detector, and a Model 717 Plus autosampler with 500-, 10^3 -, 10^4 -, and 10^5 -Å ultrastryragel columns placed in series. Chloroform was used as the eluent at a flow rate of 1.0 mL/min. The injection volume was 100 μ L, and sample concentrations were $\sim 0.5\%$ w/v. Polystyrene standards with a low dispersity (Polysciences) were used to generate a calibration curve. Data were recorded and manipulated using the Windows-based Millennium 2.0 software package.

Thermal Analysis

DSC thermograms were recorded on a DuPont DSC 912 equipped with a TA 2000 data station, using between 5 and 8 mg of sample, a heating rate of 10°C/min, and a nitrogen purge. During the first heating scan, thermograms were recorded from ambient to $\sim 210^\circ\text{C}$. Subsequently, samples were rapidly quenched from the melt with liquid nitrogen and then analyzed during a second heating scan from -60 to 200°C . The data reported for the peak melting temperature(s) (T_m) and enthalpy of fusion (ΔH_f) were taken from the first heat. Where multiple melting transitions were observed, the reported ΔH_f value was taken as the cumulative value over the entire

melting transition region. Data reported for the glass transition temperature (T_g) were taken from the midpoint of the transition in the second scan. DSC experiments where samples were cooled at 10°C min from the melt gave peak crystallization temperatures (T_c) and corresponding enthalpies of crystallization (ΔH_c). TGA were conducted from room temperature to 500°C on a Hi-Res TGA 2950 Thermogravimetric Analyzer (TA Instruments) with a heating rate of 10°C/min under nitrogen atmosphere. The onset decomposition temperatures (T_d) were taken as the intersection of the two tangents calculated by program TGA-5.0.

Powder X-ray Analysis

Wide angle X-ray scattering (WAXS) was performed using a Philips Vertical Diffractometer with Bragg–Brentano geometry and graphite diffracted beam monochromator at 40 kV/20 mA and Cu K_α radiation (1.5405 Å). A scanning speed of 2°/min with a sample interval of 0.05° was used.

Water Uptake Measurements

Polymer films (1 cm \times 2 cm \times ~ 0.1 mm) dried in a vacuum oven (<3 mmHg, 40°C , 24 h) were placed in deionized water at room temperature. After 50 h, the samples were taken out from the deionized water, excess water at film surfaces was gently removed using Kimwipes, and the films

were weighed (wet weight). The percentage of water uptake was then calculated as follows: $100 \times (\text{wet weight} - \text{dry weight}) / \text{dry weight}$.

Solubility Test

The tests were carried out at room temperature by placing approximately 50 mg of product in 5 mL of solvent, agitating using a wrist action shaker for 1 h, and then making assessments based on visual inspection.

RESULTS AND DISCUSSION

Copolymerization of DOXTC with TMC

The monomer DOXTC was successfully synthesized by the reaction of 1,3-dioxane-5,5-dimethanol with ethyl chloroformate in THF [see Scheme (1), and the Experimental Section]. Copolymerizations of DOXTC with TMC were conducted in bulk using MAO and IBAO as catalysts at either 90 or 140°C under dry argon (see Table I). For all of the entries in Table I, the polymer yields were $\geq 92\%$. Increasing or decreasing M/C from 200 to either 100 or 400 resulted in M_n values that were decreased by $> 50\%$ (data not shown). Furthermore, extending the reaction times for entries 4–6 (Table I), which had 1 : 1 monomer feeds ($f_{\text{DOXTC}}/f_{\text{TMC}}$) did not lead to higher product molecular weights (data not shown). Analyses of copolymers from entries 1–6 by GPC gave traces that were unimodal. Further analysis of these products by $^1\text{H-NMR}$ by comparison of signals at 2.07 ppm ($-\text{CH}_2-\underline{\text{CH}_2}-\text{CH}_2-$, m) and 3.82 ppm ($\text{CH}_2-\text{C}-\text{CH}_2$ in side ring, s) for TMC and DOXTC repeat units, respectively, showed that the molar composition of both $f_{\text{DOXTC}}/f_{\text{TMC}}$ and the copolymers ($F_{\text{DOXTC}}/F_{\text{TMC}}$) were identical.

TMC homopolymerization carried out under identical conditions to those given for entries 5 and 6 (140°C) gave a relatively low-molecular-weight polymer ($M_n < 10,000$). A previous report by Albertsson and Sjoling²⁰ showed that higher-molecular-weight PTMC using Al-based catalysts resulted by carrying out polymerizations well below 140°C (see Introduction). Therefore, we studied MAO-catalyzed TMC polymerization at 90°C and found that by 2 h, PTMC was obtained in 96% yield with an M_n of 81,000 g/mol (entry 1). Based on these results, MAO-catalyzed DOXTC-TMC polymerizations at 90°C were carried out for f_{DOXTC} to f_{TMC} ratios of 0 : 1, 1 : 9, and 3 : 7 (see Table I). As the DOXTC content in the monomer

feed increased from 1 : 9 to 1 : 1, the M_n decreased from 82,000 to 8,800 g/mol (see entries 2–4). However, by increasing the reaction temperature to 140°C, copolymerization of the $f_{\text{DOXTC}}/f_{\text{TMC}}$ ratio 1 : 1 by MAO (entry 5) and IBAO (entry 6) catalysis gave copolymers in high yield after only 0.5 h with M_n values of 39,000 and 47,000 g/mol, respectively. Furthermore, elevated polymerization temperatures are required to rapidly melt DOXTC (melting point $\sim 127^\circ\text{C}$) in bulk copolymerization with f_{DOXTC} to f_{TMC} ratios $\geq 7 : 3$. Therefore, copolymerizations of the f_{DOXTC} to f_{TMC} ratios 7 : 3 (entry 7) and 9 : 1 (entry 8), as well as DOXTC homopolymerization (entry 9), were carried out at 140°C; and IBAO was chosen as the catalyst.

Solubility tests carried out on DOXTC-TMC polymers prepared using f_{DOXTC} to f_{TMC} ratios $\geq 7 : 3$ (entries 7–9) showed that these products were insoluble in a wide range of solvents, including toluene, THF, chloroform, acetone, DMSO, and dimethylformamide (see Table II). In contrast, entries 1–6 were readily soluble in chloroform and DMSO. The poor solubility of the products from entries 7–9 did not permit analyses of molecular weight or composition by GPC and NMR, respectively. However, these insoluble products purified by extraction with methanol to remove residual monomer (see Experimental Section) had FTIR spectra that correspond to that expected for conversion of cyclic carbonate monomer to linear polymer. For example, the products from entries 7–9 had vibrational bands at 1748 ± 2 and $1246 \pm 2 \text{ cm}^{-1}$, which are due to $\text{C}=\text{O}$ and $(\text{O})\text{C}-\text{O}$ stretching, respectively. The wave numbers of these absorption bands are in good agreement with that expected for acyclic aliphatic carbonates.²⁵ Similarly, the product from entry 6 (F_{DOXTC} to $F_{\text{TMC}} = 1 : 1$), which has been analyzed by both ^1H - and ^{13}C -NMR (see above and below), had vibrational stretching bands at 1748 and 1245 cm^{-1} . However, corresponding absorption bands for DOXTC and TMC were observed at 1729 : 1171 cm^{-1} and 1732 : 1190 cm^{-1} , respectively.

NMR Characterization

$^1\text{H-NMR}$ (250 MHz, chloroform- d) spectral positions of DOXTC repeat units were as follows: 4.85 (O- $\underline{\text{CH}_2}$ -O in side chain, s); 4.24 ($-\underline{\text{CH}_2}-$ in main chain, m); and 3.82 ppm (C- $\underline{\text{CH}_2}$ -O in side chain, s). Inspection of $^1\text{H-NMR}$ spectra for DOXTC-TMC copolymers provided no information on repeat unit sequence distribution. Figure 1(a) shows the 62.5 MHz $^{13}\text{C-NMR}$ spectrum (in

Table II Solubility Tests^a of DOXTC-TMC Copolymers Conducted at Room Temperature

Entry No.	Toluene	THF	CHCl ₃	Acetone	DMSO	DMF
2	+	++	++	+	++	++
3	+	++	++	+	++	++
4	+	+	++	-	++	+
7	-	--	+	--	-	-
8	--	--	-	--	-	--
9	--	--	--	--	--	--

^a Symbols are as follows: ++, soluble; +, swell; -, slightly swell; --, insoluble.

chloroform-*d*) of a F_{DOXTC} to F_{TMC} 3 : 7 copolymer (entry 3) synthesized by MAO catalysis (see Table I). Assignments of TMC (T) carbon signals were based on comparison with the PTMC ¹³C-

NMR spectrum. For the carbons of DOXTC (D) repeat units, assignments were made based on calculations using data compiled from reference compounds.²⁶ Observation of the expanded spec-

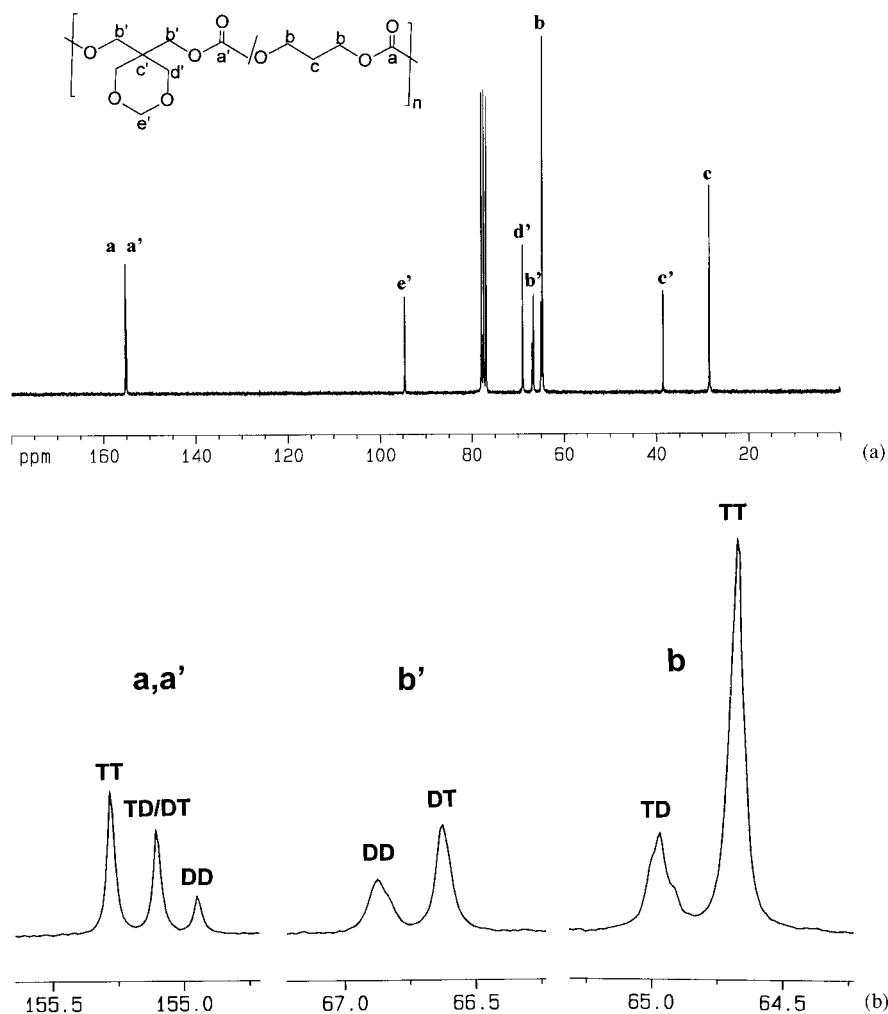


Figure 1 ¹³C-NMR (62.5 MHz) recorded in chloroform-*d* of the F_{DOXTC} to F_{TMC} 3 : 7 copolymer (entry 3): (a) the full spectrum from 0 to 180 ppm, and (b) selected expanded regions of the spectrum in 1(a), where *T* and *D* are abbreviations for TMC and DOXTC repeat units, respectively.

Table III Experimental^{a,b} and Calculated^c Comonomer Dyad Fractions

Entry	F_{DOXTC} to F_{TMC}	Dyad Sequence			Dyad Sequence			
		$\overline{\text{T-T}}$ [exptl ^a] (calcd ^c)	$\overline{\text{D-T}}$ and $\overline{\text{T-D}}$ [exptl ^a] (calcd ^c)	$\overline{\text{D-D}}$ [exptl ^a] (calcd ^c)	$\overline{\text{T-T}}$ [exptl ^b] (calcd ^c)	$\overline{\text{T-D}}$ [exptl ^b] (calcd ^c)	$\overline{\text{D-T}}$ [exptl ^b] (calcd ^c)	$\overline{\text{D-D}}$ [exptl ^b] (calcd ^c)
3	3 : 7	0.49 (0.49)	0.38 (0.42)	0.13 (0.09)	0.54 (0.49)	0.19 (0.21)	0.16 (0.21)	0.11 (0.09)
5	1 : 1	0.31 (0.25)	0.42 (0.50)	0.27 (0.25)	0.32 (0.25)	0.23 (0.25)	0.21 (0.25)	0.24 (0.25)
6	1 : 1	0.25 (0.25)	0.43 (0.50)	0.31 (0.25)	0.37 (0.25)	0.22 (0.25)	0.19 (0.25)	0.23 (0.25)

^a Determined by measuring the peak areas of ¹³C-NMR signals corresponding to carbonyl carbons a and a' [see Fig. 1(b)].

^b Determined by measuring the relative peak areas of ¹³C-NMR main chain CH₂ carbons b and b' [see Fig. 1(b)].

^c Calculated using equations that describe a Bernoullian or random statistical copolymerization.²⁷

tral regions in Figure 1(b) shows that carbons b, b', a, and a' were sensitive to effects of repeat unit sequence distribution. Variation in signal intensities for the series of copolymers differing in composition (Table I, entries 2, 3, and 5) was used to assign the ¹³C-NMR signals of carbons b, b', a, and a', which correspond to T-T, T-D, D-T, and D-D dyads [see Fig. 1(b)]. Table III gives the results for experimental and calculated dyad fractions for entries 3, 5, and 6, assuming a Bernoullian or random statistical mechanism of propagation.²⁷ Since there is good agreement between the experimental and calculated values, it was concluded that DOXTC-TMC copolymerizations catalyzed by IBAO and MAO catalysis proceed with propagation statistics that are approximately random. The random structure of TMC-DOXTC copolymers demonstrates that, in the presence of at least an equimolar ratio of TMC comonomer, DOXTC is readily polymerized by aluminoxane catalysts at both 90 and 140°C. In addition, both ¹H- and ¹³C-NMR spectra recorded for the homo- and copolymers showed no evidence for decarboxylation during polymerization. Specifically, decarboxylation would have resulted in additional signals corresponding to CH₂-O-CH₂ ether linkages [structures corresponding to ether linked dyads are shown in Scheme (2)].

Specifically, ¹H-NMR signals at ~ 3.5 ppm²⁰ and ¹³C-NMR signals between 69 (structure 3) to 74 ppm (structure 1)²⁸ were not seen but would have been observed if propagation involved decarboxylation and ether linkage formation. Other re-

ports of TMC and DTC polymerizations catalyzed by Al(O-iso-Pr)₃ and Al(O-sec-Bu)₃ that occurred without decarboxylation were described above (see Introduction) and in the literature.^{20,21}

Thermal Properties and Crystallinity

DSC was used to analyze the temperatures corresponding to copolymer glass and melting transitions (T_g and T_m , respectively). The results of DSC analyses are compiled in Table IV. The T_g of copolymers increased from -16 to 36°C as F_{DOXTC} to F_{TMC} increased from 0 : 1 to 1 : 0. The experimental data points from a plot of $1/T_g$ (K) versus DOXTC copolymer content (wt %) appeared linear (Fig. 2). Comparison of the experimental data points to the theoretical dashed line obtained by using the Fox equation²⁴ showed they were in good agreement (see Fig. 2). These results support the formation of random copolymers of DOXTC-TMC where the steric requirement of the copolymer repeat units are similar.²⁴ Copolymers with F_{DOXTC} to $F_{\text{TMC}} \leq 1 : 1$ were amorphous. In contrast, when F_{DOXTC} to F_{TMC} was $\geq 7 : 3$, the copolymers were semicrystalline. The copolymer T_m increased from 166 (upper melting peak) to ~ 202°C as F_{DOXTC} to F_{TMC} increased from 7 : 3 to 1 : 0 [see Table IV and Fig. 3(a)]. Controlled cooling (10°C min) by DSC of the polymers with F_{DOXTC} to F_{TMC} values of 7 : 3, 9 : 1, and 1 : 0 from the melt was used to study crystallization. For the F_{DOXTC} to F_{TMC} 7 : 3 copolymer, a crystallization exotherm was not observed. In contrast, the F_{DOXTC} to F_{TMC} 9 : 1 and 1 : 0 products showed crystallization exotherms with T_c 's of 130 and 142°C and ΔH_c 's of 36 and 47 J/g, respectively [see Table IV and Fig. 3(b)]. These results show that the 9 : 1 and 1 : 0 polymers readily crystallize from the melt and that higher copolymer DOXTC content leads to more rapid crystallization. Crys-

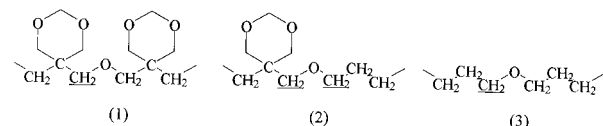
**Scheme 2**

Table IV Thermal Characterization of DOXTC–TMC Copolymers

Entry	F_{DOXTC} to F_{TMC}	T_m (°C) ^a	ΔH_f (J/g) ^a	T_c (°C) ^b	ΔH_c (J/g) ^b	T_g (°C)	T_d (°C) ^c
1	0 : 1	n/o ^d	–	–	–	–16	279
2	1 : 9	n/o	–	–	–	–11	285
3	3 : 7	n/o	–	–	–	–1	278
5	5 : 5	n/o	–	–	–	11	247
7	7 : 3	133, 166	53	n/o ^d	n/o	22	237
8	9 : 1	183, 195	65	130	36	32	238
9	1 : 0	202	75	142	47	36	223

^a Data from first heating DSC scan.

^b Peak crystallization temperature (T_c) and enthalpy of crystallization observed by DSC during cooling (10°C/min) from the melt.

^c Onset decomposition temperature (see the Experimental Section).

^d n/o is the abbreviation for “not observed.”

tallization exotherms were also observed at 125 and 109°C for the 9 : 1 and 1 : 0 products, respectively, during second heating scans after rapid cooling from the melt (see the Experimental Section). The temperatures corresponding to the onset of thermal decomposition (T_d) for DOXTC/TMC homo- and copolymers measured by TGA (see the Experimental section) were compiled in Table IV. In general, increasing the DOXTC copolymer content leads to decreased thermal stability. For example, the 1 : 9 copolymer and PDOXTC homopolymer have T_d values of 285 and 223°C, respectively. Therefore, the minimum T_m – T_d gap was 21°C for the DOXTC homopolymer (entry 9).

WAXS data was collected for the F_{DOXTC} to F_{TMC} 7 : 3, 9 : 1, and 1 : 0 homo- and copolymers. Due to the poor solubility of these polymers, measurements were made on the purified powders (see the Experimental Section). Figure 4 shows the

powder scattering data over the 2θ range from 14 to 32°. Both the 7 : 3 and 9 : 1 copolymers have WAXS patterns [Fig. 4(a) and (b), respectively] with poorly resolved crystalline reflections superimposed on amorphous haloes, indicating poorly formed crystals. The PDOXTC homopolymer [Fig. 4(c)] has more pronounced and better resolved peaks than the corresponding copolymers, indicating a higher level of crystallinity and crystalline order. This is consistent with the higher ΔH_f and T_m values of PDOXTC relative to the 7 : 3 and 9 : 1 copolymers (Table IV). The major diffraction peaks observed for PDOXTC homopolymer at $2\theta = 15.3, 16.5, 18.6, 21.3, 25.5, 27.0, 29.7,$ and 30.8° correspond to d -spacings of 5.82, 5.39, 4.76, 4.37, 3.50, 3.30, 3.01, and 2.91 Å, respectively. It is noteworthy that other 2,2-disubstituted propylene carbonates were found to be semicrystalline. Examples include poly(DTC),¹⁴ poly(NC),¹⁶ and poly(AEMC)²⁴ (see the Introduction). The latter two polymers, which have structurally dissimilar 2,2-substituents, were difficult to recrystallize from the melt during cooling DSC scans. Comparison of PDOXTC to other reported 2,2-disubstituted propylene carbonates shows that PDOXTC has the highest melting point for this family of polycarbonates. It may be that dipole–dipole interactions of 1,3-dioxane spiroconnected side groups help stabilize crystalline organizations in PDOXTC and DOXTC–TMC copolymers. Work is currently in progress to elucidate the crystal structure of PDOXTC.

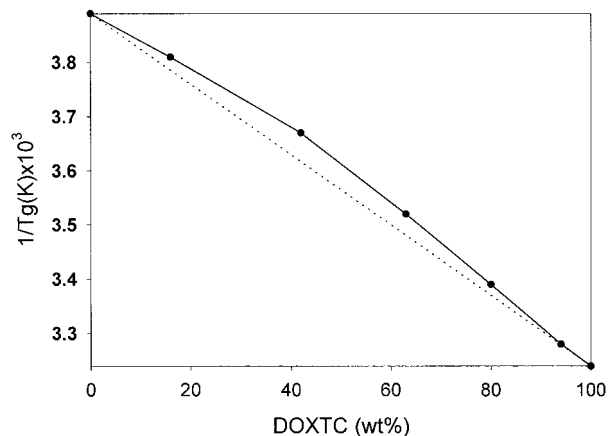


Figure 2 Plot of $1/T_g$ versus the wt % DOXTC for DOXTC–TMC copolymers of variable composition.

Water Uptake

The effects of DOXTC copolymer composition on water adsorption was investigated by immersing

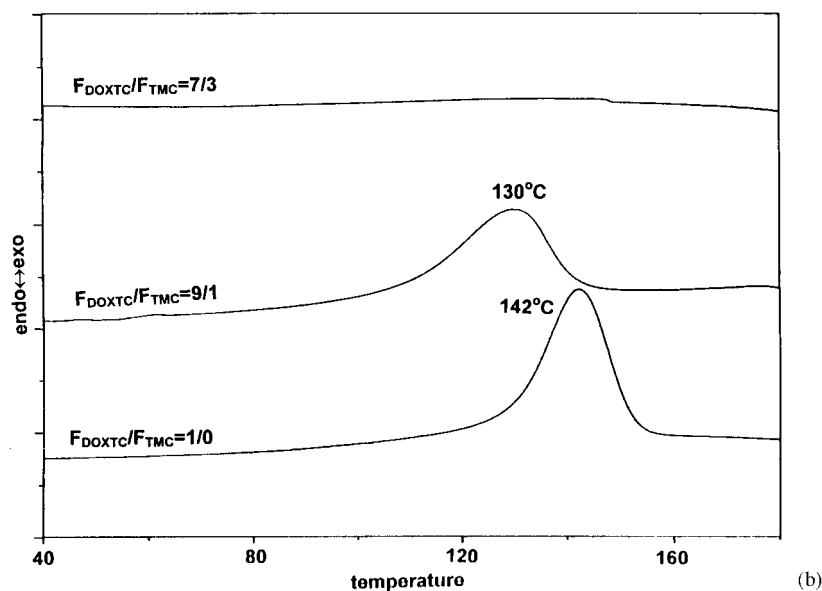
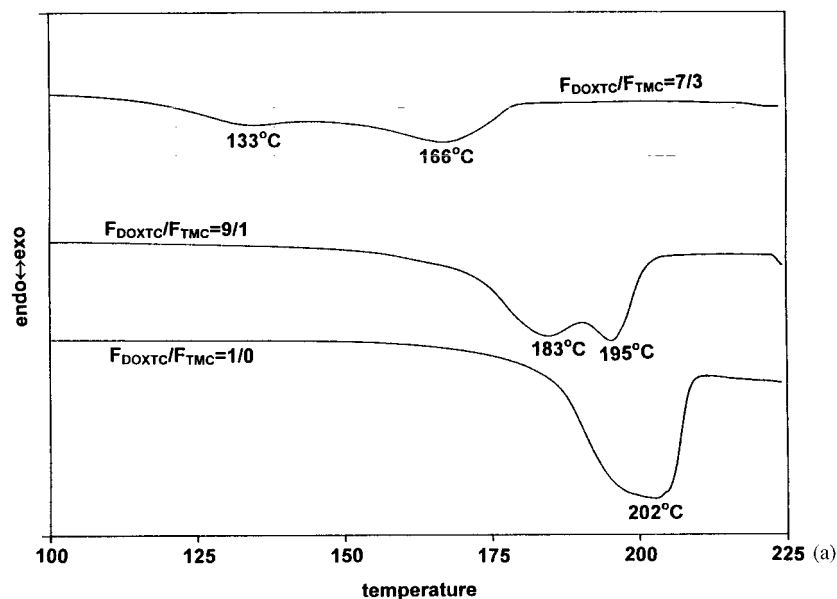


Figure 3 DSC thermograms recorded of the polymer products corresponding to entry 7 (F_{DOXTC} to F_{TMC} of 7 : 3), entry 8 (F_{DOXTC} to F_{TMC} of 9 : 1), and entry 9 (F_{DOXTC} to F_{TMC} of 1 : 0): (a) first heating scans, and (b) thermograms recorded by cooling from the melt at $10^{\circ}\text{C}/\text{min}$.

solution cast films in distilled water at ambient temperature for 50 h and measuring gravimetrically the increase in film weight. A plot of water content as a function of copolymer DOXTC wt % using product entries 1–3 and 5 in Figure 5 showed that the water content increased from 5.1 to 19% (w/w) as F_{DOXTC} to F_{TMC} increased from

0 : 1 to 1 : 1. Therefore, the introduction of 1,3-dioxane side groups by copolymerization of DOXTC with TMC is a useful strategy for increasing the film water uptake relative to PTMC. The extent that copolymer water uptake influences chain hydrolytic degradability for this copolymer series is currently under study in our laboratory.

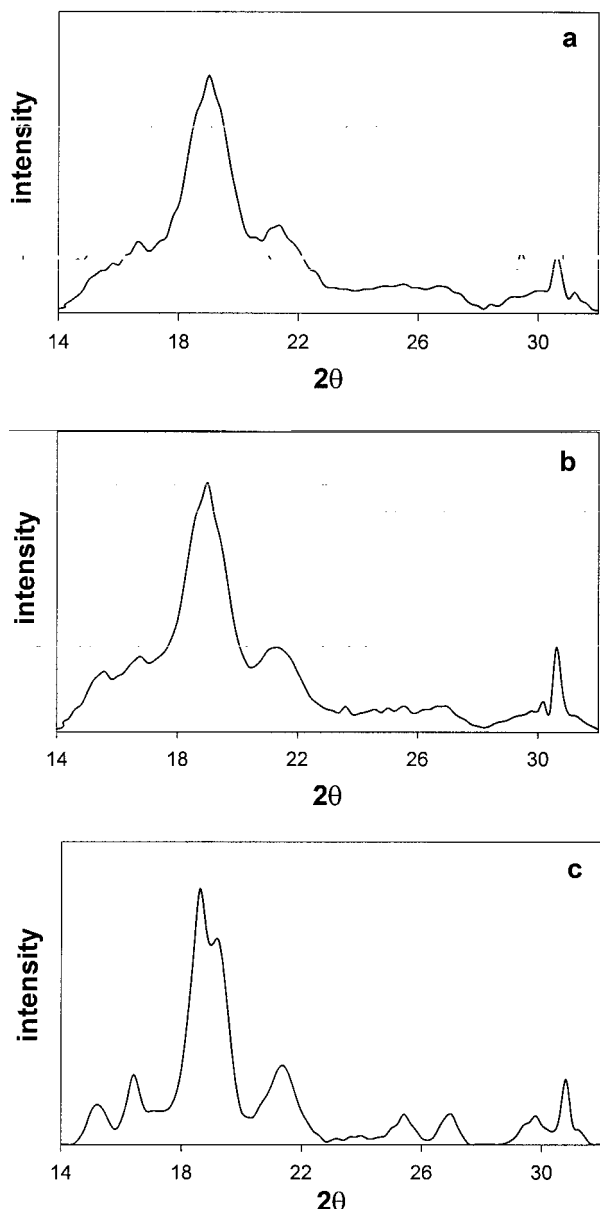


Figure 4 WAXS patterns of the polymer products corresponding to (a) entry 7 (F_{DOXTC} to F_{TMC} of 7 : 3), (b) entry 8 (F_{DOXTC} to F_{TMC} of 9 : 1), and (c) entry 9 (F_{DOXTC} to F_{TMC} of 1 : 0).

SUMMARY OF RESULTS

The new six-membered cyclic carbonate DOXTC was prepared. This monomer, when polymerized, gives spiro-1,3-dioxane side groups, which were of interest due to the size, potential to alter chain rigidity, and hydrophilicity. Homopolymerizations of DOXTC and TMC, as well as DOXTC–TMC copolymerizations, were carried out in bulk using aluminoxane catalysts. When f_{DOXTC} to f_{TMC} was $\leq 3 : 7$, polymerizations at 90°C for 2 h or

less resulted in $\geq 96\%$ polymer yields, and M_n values $\geq \sim 40,000$ g/mol. In contrast, when the DOXTC content in the monomer feed was increased to $\geq 1 : 1$, the polymerization temperature was increased to 140°C so that suitable polymer molecular weights and high polymer yields for bulk reactions in 0.5 h or less could be achieved. Copolymers prepared from f_{DOXTC} to $f_{\text{TMC}} \geq 7 : 3$ were insoluble in a wide range of organic solvents. Analyses of the DOXTC–TMC copolymers by ^{13}C -NMR showed that the copolymerizations proceeded with propagation statistics that were approximately random. Furthermore, NMR studies showed that propagation occurred without decarboxylation. DSC and WAXS showed that copolymers containing F_{DOXTC} to $F_{\text{TMC}} \geq 7 : 3$ were semicrystalline. PDOXTC had T_m and ΔH_f values of 202°C and 75 J/g, respectively. To our knowledge, this is the highest melting 2,2-disubstituted propylene carbonate polymer reported thus far. We speculated that dipole–dipole interactions of 1,3-dioxane spiroconnected side groups helped stabilize PDOXTC crystalline organizations. The WAXS pattern of PDOXTC was used to determine d -spacings. Comparison of the WAXS patterns of PDOXTC to copolymers with F_{DOXTC} to F_{TMC} of 7 : 3 and 9 : 1 showed that the former sample had more pronounced and better-resolved crystalline reflections. Therefore, PDOXTC had a higher level of crystallinity and crystalline order than the corresponding copolymers. Finally, by increasing the molar content of 1,3-dioxane side groups in DOXTC–TMC copolymers from 0 to 50%, the water uptake by the corresponding films was in-

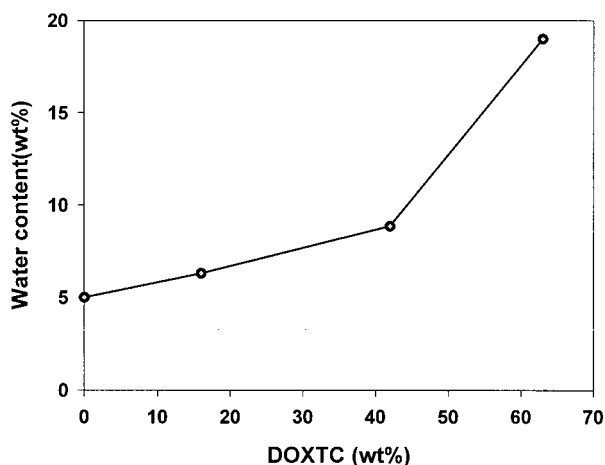


Figure 5 A plot of the film percentage of water content [$100 \times (\text{wet weight} - \text{dry weight}) / \text{dry weight}$] versus the copolymer composition (wt % of DOXTC repeat units) for films that were placed in deionized water for 50 h at 25°C.

creased from 5.1 to 19% (w/w). The results of this work will be useful for the molecular design of 2,2-disubstituted propylene carbonate polymers that have the desired physicochemical and biological properties for applications as bioerodable medical and environmentally degradable materials.

REFERENCES

1. I. M. Raigorodskii, V. S. Rabkin, and V. V. Kireev, *Vysokomol. Soedin., Ser. B*, **37**, 445 (1995).
2. M. Acemoglu, PCT Int. Appl. WO 9320126 (1993).
3. E. Chiellini, R. Solaro, and L. Bemporad, Eur. Pat. Appl. EP 486437 (1992).
4. A. R. Katz, D. P. Mukherjee, A. L. Kaganov, and S. Gordon, *Surg. Gynecol. Obstet.*, **161**, 312 (1985).
5. G. T. Rodeheaver, T. A. Powell, J. G. Thacker, and R. F. Edlich, *Am. J. Surg.*, **154**, 544 (1987).
6. T. Kawaguchi, M. Nakano, K. Juni, S. Inoue, and Y. Yoshida, *Chem. Pharm. Bull.*, **31**, 4157 (1983).
7. T. Kojima, M. Nakano, K. Juni, S. Inoue, and Y. Yoshida, *Chem. Pharm. Bull.*, **32**, 2795 (1984).
8. R. F. Storey and D. C. Hoffman, *Macromolecules*, **25**, 5369 (1992).
9. K. Soga, Y. Tazuke, S. Hosada, and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 217 (1977).
10. X. Chen, Z. Shen, and Y. Zhang, *Macromolecules*, **24**, 5305 (1991).
11. Z. Shen, X. Chen, and Y. Zhang, *Macromol. Chem. Phys.*, **195**, 2003 (1994).
12. X. Chen, Y. Zhang, and Z. Shen, *Chin. J. Polym. Sci. (Eng. ed.)*, **12**, 28 (1994).
13. H. Hocker, H. Keul, S. Kuhling, and W. Hovestadt, *Makromol. Chem., Macromol. Symp.*, **42/43**, 145 (1991).
14. H. Keul, R. Bacher, and H. Hocker, *Makromol. Chem.*, **187**, 2579 (1986).
15. T. Ariga, T. Takata, and T. Endo, *J. Polym. Sci., Polym. Chem.*, **31**, 581 (1993).
16. S. Kuhling, H. Keul, and H. Hocker, *Macromolecules*, **24**, 4229 (1991).
17. J. Matsuo, F. Sanda, and T. Endo, abstr. of paper presented at the 36th IUPAC International Symposium on Macromolecules, Seoul, Korea, August 4–9, 1996, p. 6-P01-72.
18. S. Kuhling, H. Keul, and H. Hocker, *Makromol. Chem.*, **193**, 1207 (1992).
19. H. R. Kricheldorf and B. Weegen-Schulz, *J. Polym. Sci., Polym. Chem.*, **33**, 2193 (1995).
20. A.-C. Albertsson and M. Sjoling, *Pure Appl. Chem.*, **A29**, 43 (1992).
21. P. Schmidt, H. Keul, and H. Hocker, *Macromolecules*, **29**, 3676 (1996).
22. K. J. Zhu, R. W. Hendren, K. Jensen, and C. G. Pitt, *Macromolecules*, **24**, 1736 (1991).
23. S. Kuhling, H. Keul, H. Hocker, H.-J. Buysch, and N. Schon, *Makromol. Chem.*, **192**, 1193 (1991).
24. S. Kuhling, H. Keul, and H. Hocker, *Makromol. Chem.*, **191**, 1611 (1990).
25. A. Rokicki and W. Kuran, *Rev. Macromol. Chem.*, **C21**, 135 (1981).
26. E. Pretsch, J. Seibl, W. Simon, and T. Clerc, *Tables of Spectral Data for Structure Determination of Organic Compounds*, Translated from the German by K. Biemann, F. L. Boschke, W. Fresenius, J. F. K. Huber, E. Pungor, G. A. Rechnitz, W. Simon, and T. S. West, Eds. Springer-Verlag, Berlin, 1983.
27. T. L. Bluhm, G. K. Hamar, R. H. Marchessault, A. F. Colin, and R. P. Veregin, *Macromolecules*, **19**, 2871 (1986).
28. H. N. Cheng, in *Modern Methods of Polymer Characterization*, H. G. Barth and J. W. Mays, Eds., John Wiley & Sons, Inc., New York, 1991, Chap. 11, p. 409.