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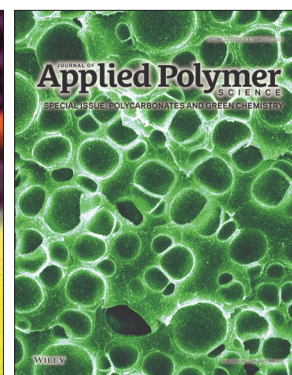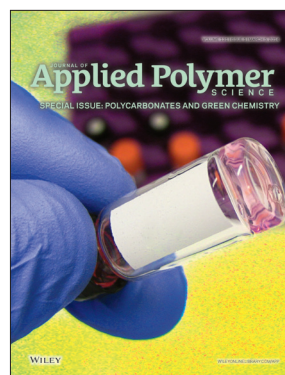
JOURNAL OF Applied Polymer SCIENCE

Synthesis of Biodegradable High Molecular Weight Polycarbonates from 1,3-Trimethylene Carbonate and 2,2-Dimethyltrimethylene Carbonate

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ABSTRACT: The possibility to obtain biodegradable high molecular weight aliphatic polycarbonates from trimethylene carbonate (TMC) and 2,2-dimethyltrimethylene carbonate (DTC) monomers with designed composition of comonomeric units was presented. Zinc(II) acetylacetonate monohydrate was used as a catalyst. A detailed analysis of copolymer chain structure was performed by means of high resolution ^{13}C-NMR spectroscopy. The equations for calculation of characteristic parameters of copolymer chain such as average length of blocks, randomization and transesterification coefficients were shown. The copolymerization reactivity ratios were determined ($r_{TMC} = 1.17 \pm 0.20$ and $r_{DTC} = 0.42 \pm 0.09$). Significant differences in the reactivity of comonomers and the low transesterification result in gradient chain microstructure. The synthesized copolymer containing about 80 mol % of DTC units is a semicrystalline material with good mechanical properties, allowing for application of this material in the formation of bioresorbable flexible implants or scaffolds. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40037.

INTRODUCTION

The trimethylene carbonate (TMC) copolymers, synthesized with glycolide, lactides, or ε-caprolactone are well-known bioresorbable materials with proven biocompatibility and visibly increasing importance in biomedicine. The incorporation of carbonate units to the main copolymer chain allows not only to obtain greater flexibility, but simultaneously reduces the acidity of degradation products.[1] This is particularly important for tissue engineering applications, because better conditions for the proliferation of cultured cells on scaffolds made from such material are possible. Mainly for this reason, trimethylene carbonate/ε-caprolactone copolymers are particularly promising materials for forming the flexible three-dimensional scaffold for cell culture.[2–6] A lot of bioresorbable polymeric materials, which have been well known for a long time, are modified at the synthesis stage by adding the aliphatic different cyclic carbonate monomers to the started reaction mixture.[7,8] The glycolide/TMC copolymers are used for production of flexible surgical sutures, which are mainly applied to soft tissue stapling, in many cases are more comfortable than typical polyglycolide or poly(glycolide-co-lactide) surgical threads.[9] Through copolymer-

ization of L-lactide with trimethylene carbonate it is also possible to eliminate the disadvantages of poly(L-lactide), such as high crystallinity and stiffness at a temperature close to the human body.[10,11] Such copolymers have been used in the formation of different temporary surgical implants, such as orthopedic fasteners, nets, nails, and surgical pins, which are commercially available today. An additional advantage of this group of aliphatic poly(ester-co-carbonates) and polycarbonates is the fact that comonomers used in synthesis are six-membered aliphatic cyclic carbonates, which can be prepared based on raw materials derived from renewable resources[12,13] or with CO_2 as a substrate.[14] Also it should be noted that six-membered cyclic carbonates are the preferred monomers for ring-opening polymerization process as in contrast to the five membered.

For these reasons, we can see that the ROP reaction of six-membered aliphatic carbonates is a very promising potential method of synthesis of biodegradable materials. With proper adjustment of the amount and kind of carbonate monomers, control over properties of obtained products is possible and new materials with unique physical parameters may be synthesized allowing to expand their potential application. From our

long-term experience we can conclude that copolymers of TMC with 2,2-dimethyltrimethylene carbonate (DTC) are especially perspective materials. The homopolymers of both six-membered cyclic monomers show significantly different properties. Poly(trimethylene carbonate) (PTMC) is a completely amorphous with glass transition temperature close to −17°C while poly(2,2-dimethyltrimethylene carbonate) (PDTC) presents typical semicrystalline properties.[15–18] Carrying out the copolymerization of mentioned comonomers, it is possible to obtain a biodegradable material with varied chain microstructure and controlled properties by proper selection of comonomer composition. To date, only two papers describe the properties of TMC/DTC copolymers, which were synthesized in the ROP way using rare earth metals complexes as initiators.[19,20] The obtained TMC/DTC copolymers have low molecular weight (average molar mass Mn no more than 10,000 g/mol),[19] much lower than expected based on theoretical calculations. Therefore these copolymers were completely amorphous or with very low degree of crystallinity. Also there is no study on the mechanical properties of the materials, which is probably connected with the difficulties in receiving sufficiently high molecular mass of the material. This is undoubtedly also the main cause of absence of examples of TMC/DTC copolymers applications in medicine and tissue engineering in literature data so far.

In this article, investigation of copolymerization of cyclic carbonates, TMC with DTC using zinc(II) acetylacetonate monohydrate as catalysts, is presented. The proper selection of the catalyst was performed taking into account the simplicity of the structure, high stability, and relatively low price, which allows for its potential industrial application. The selected compound as initiator of copolymerization possesses a high catalytic activity and good efficiency in the previously investigated TMC and DTC homopolymerizations.[18,21] In the case of this zinc complex, TMC polymerization proceeds with accordance to the mechanism of monomer activation[21,22] which allows to carry out the homopolymerization of six-membered aliphatic carbonates fast with high efficiency and with relatively high tolerance of impurities present in the reaction medium. Application of this initiator may permit to obtain TMC/DTC copolycarbonates with high molecular mass, thereby exhibiting suitable mechanical properties with good mechanical strength.

EXPERIMENTAL

Monomers and Catalyst

1,3-Trimethylene carbonate (TMC) was obtained from Boehringer (Ingelheim, Germany) and purified by recrystallization from dried ethyl acetate and then dried in a vacuum oven at room temperature. 2,2-Dimethyltrimethylene carbonate (DTC) was synthesized in two stages by transesterification of neopentyl glycol (Aldrich) with diphenyl carbonate (Aldrich) and then as a result of thermal degradation of obtained oligocarbonate. As initiator of the transesterification reaction titanium(IV) butoxide (Aldrich) was used. Crude DTC was distilled. Having rejected the first fraction, the obtained product was washed twice in cold and dry tert-butyl methyl ether (Aldrich). The obtained raw DTC was recrystallized from dry ethyl acetate. The pure DTC with the yield of 30–40% was achieved. Zinc(II) acetylacetonate

monohydrate (Alfa Aesar) was used as received. The actual water content in the complex was confirmed by measurement by TGA (METTLER—Toledo TGA/DSC Star). The amount of water as measured in the molecule, was 6.6 wt %, which is equivalent to 1.08 mol of H_2O per 1 mol of the complex.

Polymerization and Copolymerization Procedure

The monomer(s) with the appropriate amount of $Zn(acac)_2 \times H_2O$ were charged in argon atmosphere into dried glass vessel equipped with a magnetic stirrer and argon inlet, which then were sealed. Reaction was conducted at 130°C under a blanket of inert gas and with continuous stirring. After the selected reaction time, the vessel was quickly quenched to room temperature. The resulting polymers or copolymers were purified from residual monomer by dissolving in chloroform and dropwise addition of the resulting solution to cold methanol. Then, the purified material, after drying in a vacuum oven at room temperature, was subjected to further studies.

Measurements and Calculations

The number-average and weight-average molar masses (M_n and M_w, respectively) and dispersity indexes (M_w/M_n) of the polymers and copolymers were determined by gel permeation chromatography with a Viscotek RImax chromatograph. Chloroform was used as the eluent, and the temperature and the flow rate were 35°C and 1 mL/min, respectively. Two PL Mixed E columns with a Viscotek model 3580 refractive index detector were used. The molecular weights were calibrated with polystyrene standards.

Thermal properties (glass transition, temperature, and enthalpy of melting) were determined using TA DSC 2010 differential scanning calorimeter (DSC) (TA Instruments, New Castle, DE) according to ASTM and ISO standards.[23,24] The instrument was calibrated with high purity indium and gallium. The specimens of around 10 mg were heated in crimped aluminum pans (from −100 to 220°C) under a nitrogen atmosphere (flow = 50 mL/min) at heating rate of 20°C/min. The melting temperature (T_m) of samples was taken as the peak maximum of melting endotherm from first heating run at 20°C/min. Using of high scanning rates result in better sensitivity of the recorded transition.[24] To obtain the glass transition temperature the polymer was then transformed to the glassy state by cooling from melt (from 220°C) (at cooling rate of 20°C/min) to the temperature of about 50°C below glass transition temperature. Such applied fast cooling rate of 20°/min does not allow crystallization, leads to fully amorphous glassy state, and allows determine the glass transition temperature (T_g) of amorphous sample. The glass transition temperature (T_g) was next obtained from the second heating run at 20°C/min in which this is the only phenomenon revealed. The glass transition temperature (T_g) was taken as the midpoint of heat capacity change for amorphous samples.

Thermal stability of copolymers was examined by TGA with the TGA/DSC 1 METTLER TOLEDO apparatus, at a heating rate of 10°C/min under anaerobic conditions in a nitrogen atmosphere.

Mechanical testing of TMC/DTC copolymers sample tensile was performed on the testing machine "Instron" model 2402 at 23°C at a stretching rate of 20 mm/min and jaw spacing equal to 30 mm. The test samples were formed by compression using a
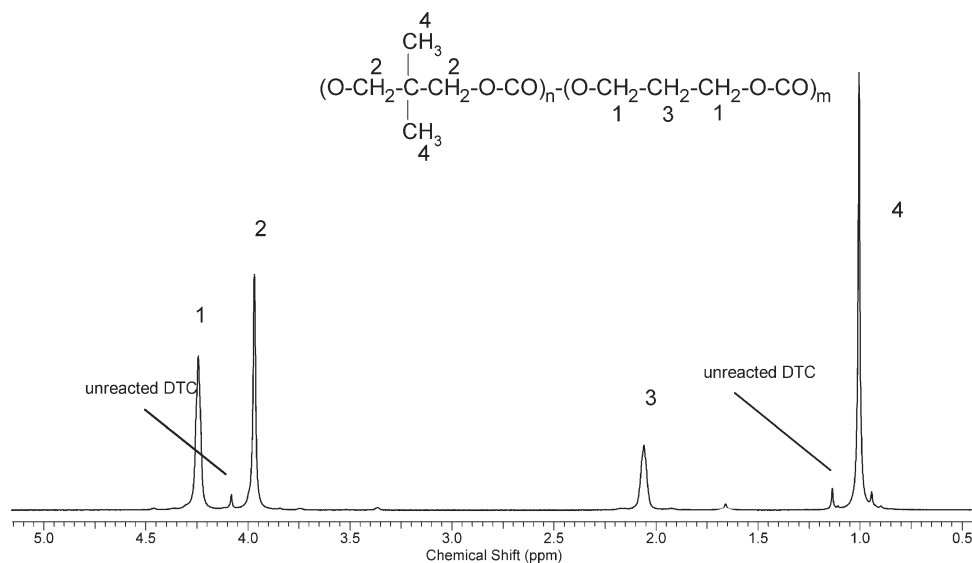
Figure 1. ^{1}H-NMR spectrum (in CDCl$_3$) of an equimolar poly(TMC-co-DTC) copolymer (full range) obtained with the use Zn(acac)$_2$ × H$_2$O as initiators.

hydraulic press. We used the mold with dimensions of the slot, 100 × 100 mm^2 and a thickness of 1 mm, at pressing temperature range from 100 to 120°C. The resulting plates were cut into strips with dimensions of 100 × 10 × 1 mm^3, which after weathering (about 2 days at room temperature) were further screened. The conversion of monomers, the composition, and microstructure of the obtained copolymers were determined by ^{1}H-NMR and ^{13}C-NMR measurements. Measurements were performed on a Bruker spectrometer AvanceTM 600 MHz using deuterated chloroform (CDCl$_3$) as solvent and tetramethylsilane (TMS) as internal standard. ^{1}H-NMR spectra were obtained after 64 scans, with 2.65 s acquisition time and 11 μs pulse width. ^{13}C-NMR spectra of the copolymers were obtained after 19,500 scans, with 0.91 s acquisition time and 9.1 μs pulse width. The copolymerization parameters were obtained with the integrated form of Skeist's copolymerization equation.[25,26] Calculation of reactivity ratios r_{TMC} and r_{DTC} was restricted not only to low monomer conversion but also was possible in binary copolymerizations from comonomer/copolymer composition data as obtained from polymerization experiments with finite monomer conversion. Above required data were received with ^{13}C-NMR spectroscopy. The usefulness of this method was previously confirmed.[27,28] The appropriate calculations were performed with a computer program named COPOINT, which was written specifically for this type of calculation.[29] For applied numerical integration technique calculations, the least-squares model was used.

RESULTS AND DISCUSSION

### Microstructure Analysis of TMC/DTC Copolymers by High-Resolution NMR Spectroscopy

^{1}H-NMR spectra were used for determination of TMC/DTC copolymer composition (Figure 1) by simple integration of methylene signals protons in TMC units (4.25 ppm) and DTC units (4.0 ppm) (Scheme 1, Figure 1).

For the determination of copolymer chain microstructure, ^{13}C-NMR spectra were used on the basis of our previous microstructure investigations of aliphatic copolyesters and copolyester-carbonates.[30,31] The spectra of the TMC and DTC homopolymers as well as the spectra of copolymers differing in the content of comonomers (20/80, 50/50, and 80/20 mol %) in the copolymer chain were compared for microstructural analysis. Figure 2 displays the ^{13}C-NMR spectrum of an equimolar TMC and DTC copolymer with ordering the main signals to appropriate methylene, methyl, carbonyl, and quaternary carbons groups of TMC and DTC units in copolymer chain. In the regions of carbonyl carbons (Figure 3), oxymethylene carbons (Figure 4) and quaternary carbon of DTC units (Figure 5) good resolved lines are visible. Previously Zhu[19] and coworkers have published ^{13}C-NMR spectrum of TMC/DTC copolymer and in carbonyl region visible lines have ordered to TMC-DTC diads. However, low molecular masses copolymers (visible end groups in ^{1}H-NMR spectra) and only copolymers with predominantly TMC units in chains were
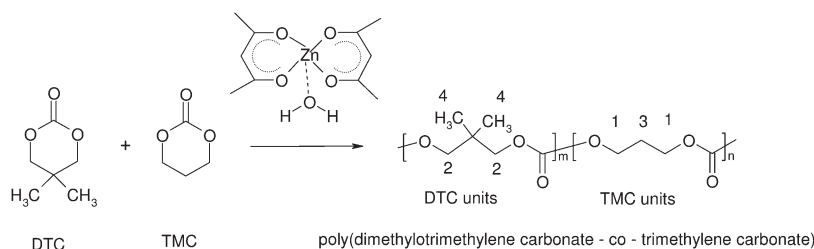

Scheme 1. Course of DTC/ TMC copolymerization.
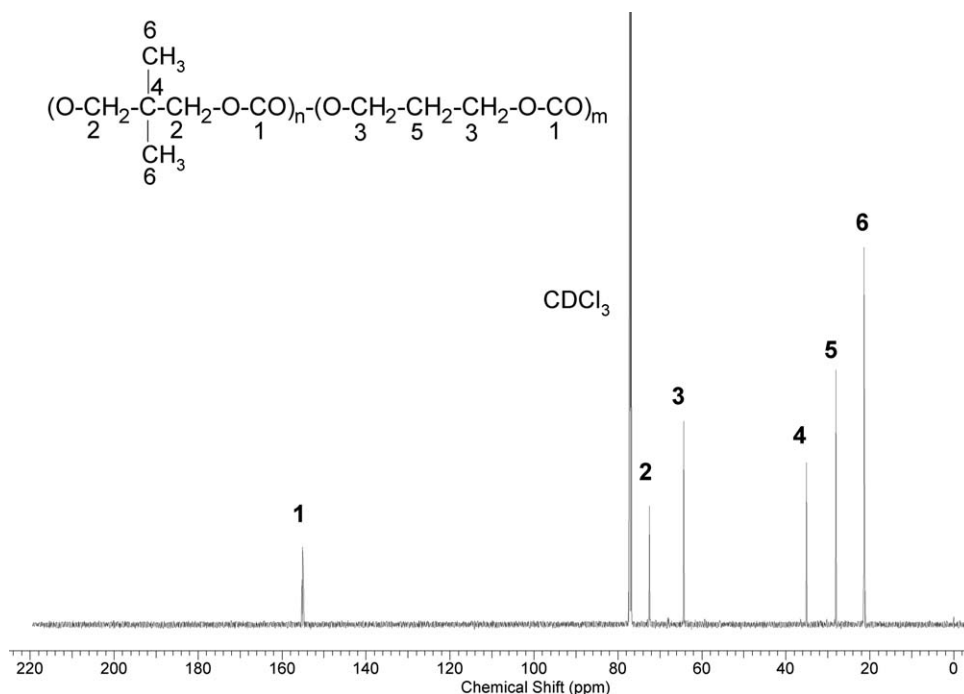
Figure 2. ^{13}C-NMR spectrum (w CDCl$_3$) of an equimolar poly(TMC-co-DTC) copolymer (full range) obtained with the used Zn(acac)$_2$ × H$_2$O as initiators.

analyzed (highest amount of DTC units in chain was 41 mol %). Our investigations on the basis of comparison of all copolymer samples clearly show that in all regions lines from triads sequences are visible (Figures 3–5) and unequivocal assignment of the resonance lines to appropriate comonomeric triads is possible (Table I).
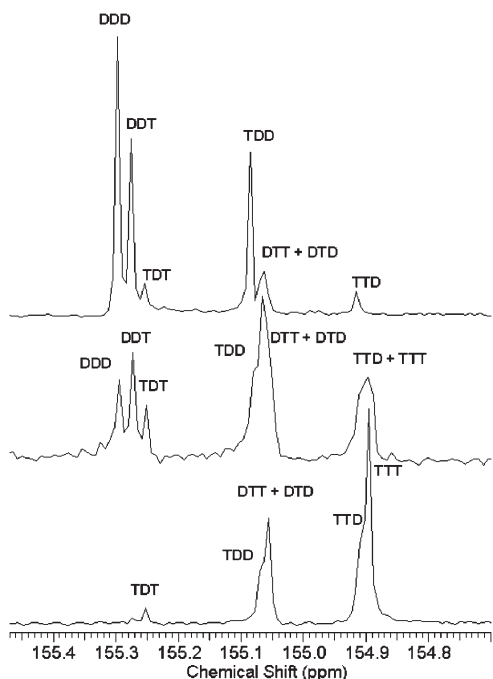
Figure 3. ^{13}C-NMR spectra of TMC/DTC copolymers (range of carbonyl carbons) obtained with Zn(acac)$_2$ × H$_2$O and about (A) 20 mol % TMC, (B) 50 mol % TMC, (C) 80 mol % TMC.

On the basis of triads intensities average lengths of carbonate TMC and DTC units were calculated using the eqs. (1) and (2).

$$L_T^e = \frac{[TTT]+[TTD]+[DTT]+[DTD]}{[DTD]+\frac{1}{2}\left([TTD]+[DTT]\right)} \tag{1}$$

$$L_D^e = \frac{[DDD]+[DDT]+[TDD]+[TDT]}{[TDT]+\frac{1}{2}\left([DDT]+[TDD]\right)} \tag{2}$$

To verify the correctness of the calculations, eq. (3) may be used.

$$L_D^e = L_T^e \frac{1-N_T}{N_T} \tag{3}$$

where N_T is a molar fraction of TMC units in the copolymer.

The average lengths of TMC – (L_T^R) and DTC (L_D^R) blocks in chains with completely random distribution of carbonate units were calculated using eqs. (4) and (5)
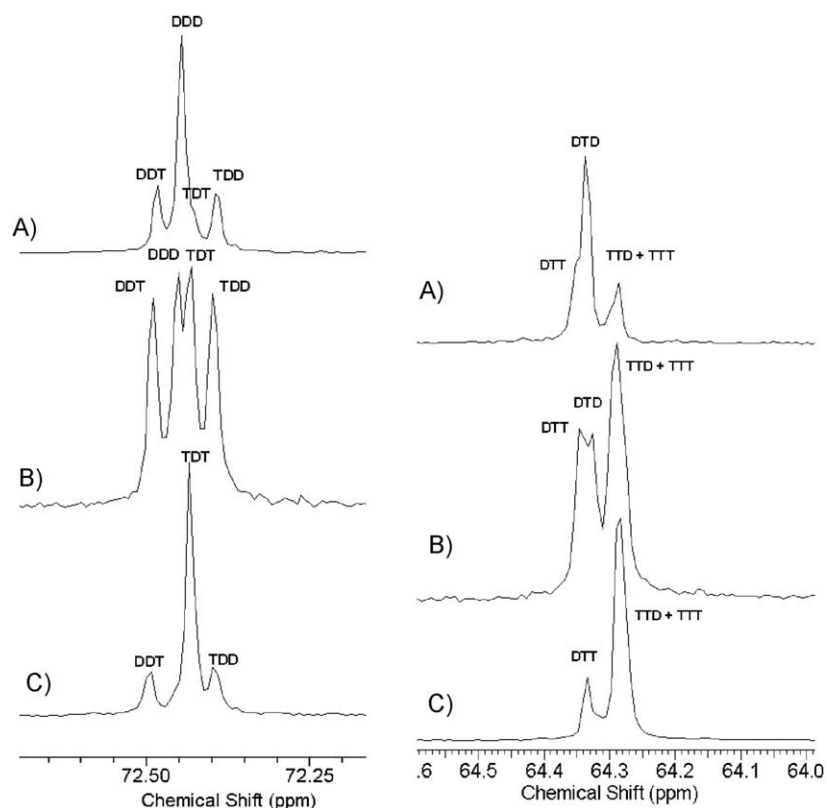
$$L_T^R = 1/(1-N_T) \tag{4}$$

$$L_D^R = 1/N_T \tag{5}$$

The degree of randomness of copolymer chains (R) can be calculated from the following eq. (6).

$$R = L_T^R/L_T^e = L_D^R/L_D^e \tag{6}$$

Examination of the Chain Growth of TMC/DTC Equimolar Copolymer

The course of chain propagation with the progress of the copolymerization reaction of TMC with DTC on the example

Figure 4. ^{13}C-NMR spectra of TMC/DTC copolymers (range of oxymethylene carbons) obtained with Zn(acac)$_2 \times$ H$_2$O and about (A) 20 mol % TMC, (B) 50 mol % TMC, (C) 80 mol % TMC.

of initial equimolar reaction mixture was examined. The received data are presented in Table II. The rate of the investigated reaction was rather high and after about 30 min, nearly total conversion of both comonomers was observed (Figure 6).

Copolymerization reactivity ratios were determined using COPOINT,[29] on the basis of the data obtained from measurements of the degree of conversion of each monomers and composition of the copolymer samples taken after various times of ongoing reaction. Each sample was prepared with parallel reactions, conducted in the same conditions, quenched in turn after planned time. TMC monomer showed higher reactivity compared to DTC (Figure 7).

The estimated monomers reactivity were, respectively; $r_{TMC} = 1.17 \pm 0.20$ and $r_{DTC} = 0.42 \pm 0.09$. The difference in reactivities between the comonomers was significantly lower in comparison with the differences in reactivity of the comonomers listed for the majority of previously studied copolymerizations of TMC with lactides[28,31] as well as analogous copolymerization of TMC with DTC performed with rare earth metal complexes.[19] Similar differences between comonomers reactivity ratios have been observed during copolymerization of TMC with ε-caprolactone conducted with zirconium initiator,[30] but chain microstructure of this copolymer was completely different (close to random) because of strong transesterification processes which occurred in this case.

Using the determined monomers reactivity ratio it is possible to estimate the theoretical (calculated) DTC and TMC average

length of blocks (L^r_{DTC}, L^r_{TMC}) with the use of eqs. (7) and (8) describing the dependence between monomers reactivity ratio, copolymer composition and average lengths of copolymers microblocks.[32] This dependence was used and proven earlier.[28,30]

$$(L^r_D)^2 \times \frac{1-N_D}{N_D} - L^r_D x = r_{DTC} \times r_{TMC} \quad (7)$$

$$(L^r_T)^2 \times \frac{1-N_T}{N_T} - L^r_T x = r_{DTC} \times r_{TMC} \quad (8)$$

Upon determination of the average length values of copolymer microblocks on the basis of monomers reactivity ratios (L^r_T, L^r_D), experimental length values of carbonate microblocks (L^e_T, L^e_D) and calculated average length values of blocks in chains with completely random contribution (L^R_T) (L^R_D) we can estimate the ratio of the intermolecular transesterification (T), which proceeds during main copolymerization reaction using the following sequences eqs. (9) and (10):

$$T = \frac{L^r_D - L^e_D}{L^r_D - L^R_D} \quad (9)$$

$$T = \frac{L^r_T - L^e_T}{L^r_T - L^R_T} \quad (10)$$

The experimental results and average values of block length determined from reactivity ratios (Table II) indicate that during the reaction of propagation the TMC monomer is initially incorporated to the copolymer chain and towards the end of
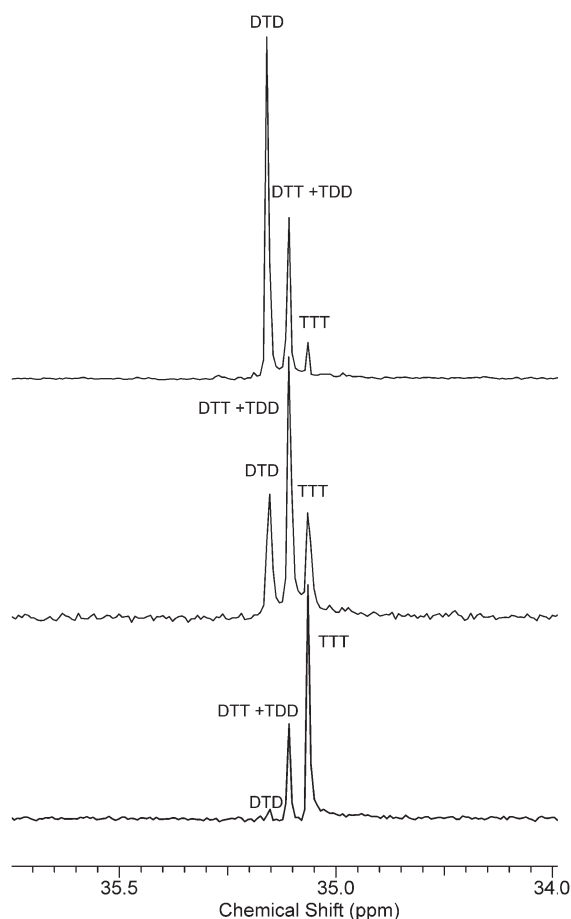
Figure 5. ^{13}C-NMR spectra of TMC/DTC copolymers (range of quaternary carbons) obtained with $Zn(acac)_2 \times H_2O$ and about (A) 20 mol % TMC, (B) 50 mol % TMC, (C) 80 mol % TMC.

Table I. Assignment of the Resonance Line in the ^{13}C-NMR Spectrum (in $CDCl_3$) of TMC/DTC Copolymer, Where T, TMC Units—$O(CH_2)_3O(CO)$ and D, DTC Units—$O(CH_2)_3(CH_3)_2O(CO)$

Comonomer sequences		Signal δ ppm
Carbonyl carbon region, DTC i TMC units		
1	DDD	155.27
2	DDT	155.25
3	TDT	155.24
4	TDD	155.08
5	DTT + DTD	154.04
6	TTT + TTD	154.90
Methylene carbon region, DTC units		
7	DDT	72.47
8	DDD	72.42
9	TDT	72.40
10	TDD	72.36
Methylene carbon region, TMC units		
11	DTT	64.34
12	DTD	64.33
13	TTD + TTT	64.28
Quaternary carbon region, DTC units		
14	DTD	35.16
15	DTT + TTD	35.09
16	TTT	35.05

reaction to DTC monomer. It was confirmed by progress of monomers conversion (Figure 7).

Simultaneously the calculated transesterification coefficients T take values much lower than 1 (e.g., TMC/ε-caprolactone copolymerization[30] coefficients T were close to 1 and R affiliated with randomness of chain was significantly above 1). This indicates, taking into account average block length measurement error, a low influence of the transesterification reaction on the final copolymer chain microstructure. In the synthesis of completely random copolymer ($r_{TMC} = r_{DTC} = 1$), the average length of both the TMC and DTC blocks equals 2. In fact, the chain microstructure of the synthesized copolymer was very close to completely random, as evidenced by the calculated coefficient of randomization (R) which is only slightly below 1 (final average block length only a little higher than 2). The presence of only one glass transition temperature confirms the postulated chain microstructure distant from the block structure, too. However, it should be noted that the microstructure of the copolymer chain is not typically random, because noticeable difference between comonomers reactivity and a low degree of transesterification can be observed. The structure of the copolymer chain must be a gradient, where one end of the chain contains the majority of TMC units sequences, and the other is formed with

a predominance of the longer DTC units sequences. Analogous phenomenon of creating a gradient copolymer chain structure was described in the case of D, L-lactide/ε-caprolactone copolymer obtained in the presence of an aluminum salen complex[33] where copolymerization reactivity ratios achieved values close to those identified in the submitted study.

**Effect of Composition on Copolymer Chain Structure**

To characterize the effect of comonomer composition on the properties of the obtained copolymers and final structure of the copolymer chain, a series of copolymerization reactions were conducted, performed under the same conditions and with the same amount of the initiator, which was $Zn(acac)_2 \times H_2O$. The obtained results are presented in Table III. In a relatively short time, we have received high molecular weight copolymers with high yield, consistent with the assumed composition of monomers. Along with the increasing of DTC content in the initial mixture of comonomers noticeable increase of the time reaction required to complete conversion was noted, which was associated with a lower reactivity of this comonomer. Given the very similar chemical structures of the cyclic carbonates and a relatively high reaction rate and monomers conversion, the mechanism of initiation and the course of copolymerization probably runs this same manner as for TMC homopolymerization in accordance to activated monomer mechanism.[21]

We observed that, regardless of the composition of the copolymer, experimental average length of carbonate TMC and DTC blocks were very similar to calculated, taking into account the
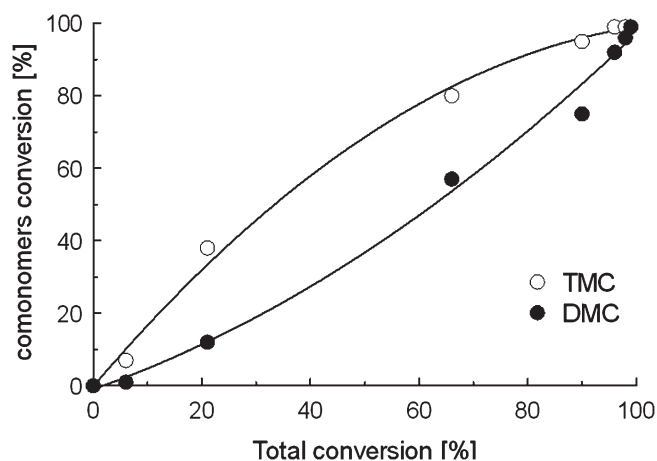
Table II. The Chain Propagation Process of Poly(TMC-*co*-DTC) (50 : 50) Obtained in the Presence of Zn(acac)$_2$ × H$_2$O as Initiator, at 130°C with Monomer/Initiator Ratio M/I = 800 : 1

No	Time (min)	C_{TMC} (%)	C_{DTC} (%)	C (%)	N_T (%)	L_T^e	L_D^e	L_T^r	L_D^r	T	R
1	1.5	5	1	6	83	2.9	1.6	3.0	1.7	0.3	0.9
2	5	74	57	66	56	2.4	1.8	2.5	1.9	0.5	0.9
3	10	95	75	87	55						
4	15	99	92	96	52	2.1	2.0	2.3	2.1	0.5	1.0
5	40	99	96	98	51	2.1	2.1	2.2	2.2	0.5	0.9
6	60	99	98	99	50	2.1	2.1	2.2	2.2	0.5	0.9

Where: C_{TMC}, conversion of TMC; C_{DTC}, conversion of DTC; C, total conversion; N_T, molar fraction of TMC units in copolymer; L_T^e, L_D^e, experimental average length of carbonates blocks, calculated from NMR spectra; L_T^r, L_D^r, determined average length of carbonates block from reactivity ratios; T, transesterification coefficient; R, randomness of the chain.
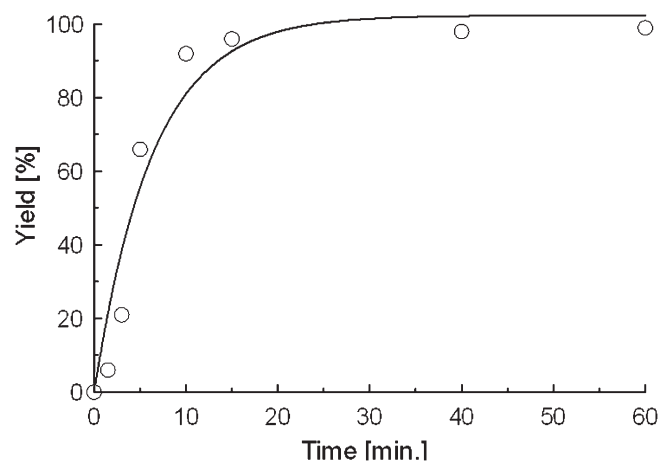
Figure 6. Total conversion of monomers in copolymerization of equimolar mixture of TMC with DTC, initiated with Zn(acac)$_2$ × H$_2$O with M/I ratio as 800 : 1 and performed in bulk at 130°C.

Figure 7. Dependence of the TMC and DTC conversion on the total conversion of the copolymerization. The starting TMC/DTC molar ratio was of 1 : 1, M/I ratio as 800 : 1, performed in bulk at 130°C.

pre-designated individual comonomer reactivity ratios. These results confirm earlier observations and testify that the microstructure of the chain is practically only dependent on the composition of initial reaction mixture and comonomers reactivity ratios. Participation of possible intermolecular transesterification reactions in the course of the investigated process is very low.

For all studied copolymers values of randomization ratio of chain (R) is near 1, but the distinct differences in reactivity ratios and practically the lack of transesterification implies gradient microstructure of the obtained copolymers. In consequence, longer blocks of monomeric units are presented in copolymer chain. In cases where these long blocks are created

Table III. Ring-Opening Copolymerization of TMC and DTC Perfomed in Bulk at 130°C, Initiated by Zn(acac)$_2$ × H$_2$O (Initiator/Monomers Molar Ratio of 1 : 800).

No.	(TMC : DTC)^O (mol %)	t (min)	Conv. (%)	(TMC : DTC)^N (mol %)	Mn × 10^{-3} (Da)	D	L_T^e	L_D^e	L_T^r	L_D^r	L_T^R	L_D^R	R
1	100 : 0	6	~100	100 : 0	102	2.0	–	–	–	–	–	–	–
2	80 : 20	30	~100	80 : 20	64	2.0	5.3	1.3	5.4	1.4	5.2	1.3	1
3	50 : 50	40	99	51 : 49	50	1.9	2.1	2.1	2.2	2.2	2.0	2.0	0.9
4	20 : 80	40	99	20 : 80	68	1.9	1.3	5.2	1.4	5.4	1.3	5.2	1
5	0 : 100	80	98	0 : 100	47	2.3	–	–	–	–	–	–	–

Where: (TMC : DTC)^O, initial feed molar fraction TMC and DTC; Conv., total conversion of copolymerization; (TMC : DTC)^N, molar fraction of TMC and DTC units in copolymer, M_n, number average molecular mass determined by GPC and calibrated with polystyrene standards; D, M_W/M_n, molecular mass dispersion; L_T^e, L_D^e, experimental average length of carbonates blocks, calculated from NMR spectra; L_T^r, L_D^r, determined average length of the carbonates blocks calculated from reactivity ratios; L_T^R, L_D^R, calculated average length of carbonates blocks for completely random contributions of TMC and DTC units in copolymer chain; R, randomness coefficient.

Table IV. Thermal and Mechanical Properties of Poly(TMC-*co*-DTC)

No.	(TMC : DTC)^N (mol %)	T_g (°C)	T_T^F (°C)	T_m (°C)	ΔH_m (J/g)	$T_{10\%}$ (°C)	T_{max} (°C)	E (MPa)	σ_{max} (MPa)	ε_{max} (%)	σ_{break} (MPa)
1	0 : 100	−1.2	-	125	42						
2	20 : 80	6.9	−3.0	73	26.4	280	310	141	12	390	8
3	51 : 49	−2.8	−5.8	-	-	260	320	7.1	0.4	93	0.4
4	80 : 20	−8.6	−8.3	-	-	280	340	2.5	0.3	100	0.2
5	100 : 0	−10.1	-	-	-						

Where: T_g, glass-transition temperature (second scan); T_T^F, glass-transition temperature calculated with Fox equation[33]; T_m, melting temperature (first scan); ΔH_m, melting endotherm (first scan); $T_{10\%}$, temperature of 10% degradation; T_{max}, the decomposition temperature; E, Young's modulus; σ_{max}, σ_{break}, maximum tensile stress, tensile stress at break, ε_{max}, maximum tensile strain.

with DMC units, during application of started copolymerization mixture with proper DMC excess, crystalline domains can be formed (Table III, row 4).

Thermal and Mechanical Properties of the Obtained Copolymers

Using differential scanning calorimetry (DSC), thermal property analysis of TMC/DTC was performed (Table IV, Figure 8).

Despite the similar chemical structure of TMC and DTC monomers, homopolymers of these cyclic carbonates represent different mechanical and thermal properties. PTMC is a flexible amorphous polymer with a glass transition temperature of about −10°C, while PDTC is a partially crystalline polymer, showing a glass transition temperature of about −1°C. Our studies (Figure 8) confirmed the two melting points at 110 and 125°C for PDTC related to the presence of distinct crystalline domains, previously observed by Keül et al.[34] On the thermogram of poly(TMC-*co*-DTC) containing 80% of DTC (Figure 8B, first heating run), there is also a melting area visible, connected with semi-crystallinity of the copolymer, as in the case of the PDTC, has a bimodal nature with the values of melting points of about 51 and 74°C. Practically all TMC/DTC

random copolymers received earlier were amorphous. Low crystallinity was exhibited only by copolymer containing about 92 mol % of DTC units.[19] It can be assumed that this effect was associated with significantly lower molar masses of these copolymers and its highly randomized chain structure. Determined glass transition temperature T_g of the copolymer with 80% mol DTC units, about 7°C (Figure 8B, second heating run), is higher than the transition temperature calculated on base the corresponding Fox equations.[35] However, in the case of the other copolymers with lower content of DTC units, completely amorphous, these values were close to calculated transition temperature. This effect is probably associated with presence of crystalline phases and their impact on the copolymers glass transition behavior.[36]

Table IV shows also the results of tensile test of specimens formed with TMC/DTC copolymers obtained with the participation of zinc acetylacetonate. The best mechanical properties showed semicrystalline copolymer with 80 mol % of DTC units. Decreasing the content of DTC units of the copolymer, we observed a significant deterioration in strength; stress value at break from 12 MPa decreased to 0.3 MPa, and the value of elongation at break from 390% to about 100%. The
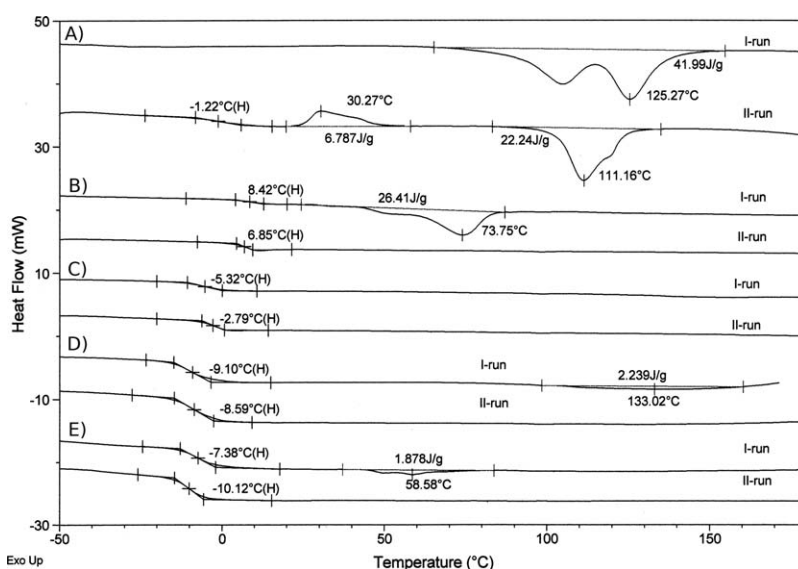
Figure 8. DSC thermograms (I and II run, respectively) of (A) PDTC and DTC/TMC copolymers contained: (B) about 20 mol % of TMC (C) about 51 mol % of TMC; (D) about 80% mol of TMC and (E) PTMC.

thermogravimetric studies indicate that poly(TMC-*co*-DTC), obtained with the described method, show high thermal stability, allowing relatively easy processing of such materials.

CONCLUSIONS

Receiving biodegradable high molecular weight trimethylene carbonate with 2,2-dimethyltrimethylene carbonate copolymers with designed composition in a relatively short time is possible by ROP reaction catalyzed by zinc(II) acetylacetonate monohydrate. The simple zinc complex used in the copolymerization turned out very effective. High molecular copolymers, synthesized with the zinc catalyst, demonstrate significantly different properties in comparison with previously received low molecular copolymers.[19] It seems that the main cause of observed possibility of obtaining high molecular TMC/DTC copolymers with application of zinc acetylacetonate catalyst is a different course of initiation and chain propagation processes compared to the same copolymerization catalyzed with rare earth complexes. Using $Zn(acac)_2 \times H_2O$ as catalyst, TMC/DTC copolymerization runs in accordance with the ROP mechanism by activating the cyclic carbonate monomers which allows to perform the reaction fast with relatively high tolerance of impurities possibly present in the reaction medium. It is also important to point out the observed good thermal stability of the TMC/DMC copolymers obtained by us and a relatively short reaction time of its synthesis, which minimalizes the influence of thermal degradation on the molecular weight of the final product.[22] The detected practical absence of transesterification processes during main reaction of copolymerization signify there is no coparticipating back-biting reaction either. This way, through radical reduction of side reactions, obtaining TMC/DMC copolymers with high average molecular mass, many times higher than previously synthetized, was possible. Not without practical importance is also the fact that used zinc catalyst is commercially easily available, relatively inexpensive and low toxic.

A detailed analysis of copolymer chain structure is possible using high resolution ^{13}C-NMR spectroscopy. Comonomeric triad sequences are as well visible in carbonyl, methylene and quaternary carbon signals. The copolymer chain microstructure is essentially dependent only on monomer reactivity ratios and comonomers content. The presence of intermolecular transesterification process has not been completely ruled out, but the influence of transesterification on the final structure of created chains is practically unnoticeable. Small but significant difference of comonomers reactivity and low contribution of transesterification reactions determine the final gradient copolymers chain microstructure. Consequently, longer blocks of monomeric units are present in copolymer chain, which results in a possibility of formation of crystalline domains of DTC units. In the case of using rare earth calixarene complexes as a catalyst of the copolymerization, differences in the reactivity of comonomers were significantly higher ($r_{TMC} = 4.68$ and $r_{DTC} = 0.16$), but nevertheless semicrystallinity showed only copolymers containing less than 8 mol % of TMC units.[19] The noted phenomenon was clearly associated with the course of the strong transesterification reactions occurring parallel to the main process of copolymerization, resulting in randomization of the final structure of the chain. Copolymers obtained by us with zinc catalyst, containing about even 20 mol % of TMC units were semicrystalline materials with good mechanical properties allowing its use in medicine in formation of bioresorbable implants and looks as especially promising as material for flexible scaffolds production.

REFERENCES

1. Jie, C.; Zhu, K. J.; Shilin, Y. *Polym. Int.* **1996**, *41*, 369.

2. Bat, E.; Plantinga, J. A.; Harmsen, M. C. M.; van Luyn, J. A.; Zhang, Z.; Grijpma, D.; Feijen, W. *J. Biomacromolecules* **2008**, *9*, 3208.

3. Pêgo, A. P.; Zhong, Z.; Dijkstra, P. J.; Grijpma, D. W.; Feijen, J. *Macromol. Chem. Phys.* **2003**, *204*, 747.

4. Schappacher, M.; Fabre, T.; Mingotaud, A. F.; Soum, A. *Biomaterials* **2001**, *22*, 2849.

5. Zhao, B.; Lu, C. R.; Shen, Q. *J. Appl. Polym. Sci.* **2007**, *106*, 1383.

6. Martina, M.; Hutmacher, D. W. *Polym. Int.* **2007**, *56*, 145.

7. Li, Z.; Yan, G.; Ai, Ch.; Zhang, Q.; Li, L.; Liu, F.; Yu, X.; Zhao, B. *J. Appl. Polym. Sci.* **2012**, *124*, 3704.

8. Chen, X.; McCarthy, S. P.; Gross, R. A. *J. Appl. Polym. Sci.* **1998**, *67*, 547.

9. Middleton, J. C.; Tipton, A. J., *Biomaterials* **2000**, *21*, 2335.

10. Andronova, N.; Albertsson, A. Ch. *Biomacromolecules* **2006**, *7*, 1489.

11. Ruckenstein, E.; Yuan, Y. *J. Appl. Polym. Sci.* **1998**, *69*, 1429.

12. Darensbourg, D. J.; Moncada, A. I.; Wilson, S. J. In Materials, Catalysis and Waste Reduction; Mathers, R. T.; Meier, M. A. R., Eds.; Wiley-VCH Verlag GmbH & Co.: Weinheim, **2011**, pp 165–197.

13. Bornadel, A.; Hatti-Kaul, R.; Sörensen, K.; Lundmark, S.; Pyo, S. H. *Biotechnol. Prog.* **2013**, *29*, 66.

14. Darensbourg, D. J.; Jrand, A. H. *Green Chem.* **2010**, *12*, 1376.

15. Pêgo, A. P.; van Luyn, M. J. A.; Brouwer, L. A.; van Wachem, P. B.; Poot, A. A.; Grijpma, D. W.; Feijen, J. *J. Biomed. Mater. Res. Part A* **2003**, *67*, 1044.

16. Pêgo, A. P.; Grijpma, D. W.; Feijen, J. *Polymer* **2003**, *44*, 6495.

17. Rokicki, G. *Prog. Polym. Sci.* **2000**, *25*, 259.

18. Dobrzynski, P.; Pastusiak, M.; Bero, M. *J. Polym. Sci.: Part A* **2005**, *43*, 1913.

19. Zhu, W.; Ling, J.; Xu, H.; Shen, Z. *Polymer* **2005**, *46*, 8379.

20. Ling, J.; Shen, Z. Q.; *Macromol. Chem. Phys.* **2002**, *203*, 735.

21. Pastusiak, M.; Dobrzynski, P.; Kaczmarczyk, B.; Kasperczyk, J. *J. Polym. Sci. Part A* **2011**, *49*, 2504.

22. Helou, M.; Miserque, O.; Brusson, J. M.; Fran, J.; Carpentier, L.; Guillaume, S. M. *ChemCatChem* **2010**, *2*, 306.

23. ASTM E 1356-08 Standard, Standard test method for assignment of the glass transition temperatures by differential scanning calorimetry, *Book of Standards Volume*: 14.02.

24. ISO 11357-3:2011 Standard, plastics—differential scanning calorimetry (DSC) - Part 3: Determination of temperature and enthalpy of melting and crystallization, *Standards Catalog: ISO/TC 61/SC 5*.

25. Skeist, I. *J. Am. Chem. Soc.* **1946**, *68*, 1781.

26. Meyer, V. E.; Lowry, G.G. *J. Polym. Sci. Part A: Gen. Pap.* **1965**, *3*, 2843.

27. Van den Brink, M.; Van Herk, A.; German, A. *J. Polym. Sci. Part A* **1999**, *37*, 3793.

28. Dobrzynski, P.; Kasperczyk, J. *J. Polym. Sci. Part A* **2006**, *44*, 3184.

29. Beginn, U. *e-Polymers*, **2005**, no. 073.

30. Dobrzynski, P. *Polymer* **2007**, *48*, 2263.

31. Dobrzynski, P.; Kasperczyk, J. *J. Polym. Sci. Part A* **2006**, *44*, 98.

32. Koening, J. L. Chemical Microstructure o Polymer Chains; Wiley: New York, **1980**.

33. Nomura, N.; Akita, A.; Ishii, R.; Mizuno, M. *J. Am. Chem. Soc.* **2010**, *132*, 1750.

34. Keül, H.; Höcker, H.; Leitz, E.; Ott, K.-H.; Morbitzer, L. *Makromol. Chem.* **1988**, *189*, 2303.

35. Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.

36. Kim, J. H.; Min, B. R.; Kang, Y. S. *Macromolecules* **2006**, *39*, 1297.