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Characterization of Polyether and Polyester Homo- and Copolymers Prepared by Ring Opening Polymerization with a New Catalytic System

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ABSTRACT: The ring-opening homopolymerization of tetrahydrofuran and ϵ-caprolactone and copolymerizations of tetrahydrofuran/ϵ-caprolactone and γ-butyrolactone respectively with a catalytic system consisting of phosphorus tricyanide and acetonitrile were studied. The homopolymers obtained were characterized by their molecular weights $\overline{M}_w$, infrared spectra, differential scanning calorimetry (DSC) behavior, and x-ray diffraction patterns. The poly(ether ester) copolymers contained approximately 3% γ-butyrolactone and 5% ϵ-caprolactone units, as determined by NMR. The copolymers were further characterized by their infrared spectra, DSC, and x-ray diffraction data.

The vigorous activities in the field of polyether and polyester ring opening polymerization are reflected in the considerable number of patents and papers published in this area.[2-11] Recently the results of tetrahydrofuran (THF) polymerization with a new catalytic system have been reported.[12] It was shown that in the presence of acetonitrile, phosphorus tricyanide, $P(CN)_3$, changes from off-white, when freshly prepared, through yellow to orange, on standing in a sealed vessel. This orange-yellow form of $P(CN)_3$ was shown to be an active catalyst in the bulk polymerization of THF to high molecular weight products.[12] Although the active species of this catalyst system is not yet fully understood owing to its complex nature, we have tested its applicability to other ring-opening polymerizations. Thus, the catalyst has been employed in polymerization reactions with ϵ-caprolactone and THF/ϵ-caprolactone as well as THF/γ-butyrolactone mixtures. The purpose of this paper is to report in some detail on the characterization of the products obtained.

Experimental Section

Viscosities were determined in Cannon Fenske viscometers at 303 K. IR spectra were recorded on a Perkin-Elmer 521 spectrophotometer and proton magnetic resonance spectra were obtained with a Jeol 4H 100S NMR spectrometer at 100 MHz on $CDCl_3$ solutions. Differential scanning calorimetry traces were obtained on a Perkin-Elmer DSC-2 calorimeter and the x-ray diffraction diagrams were recorded on a Philips goniometer PW 1050/25 (40 kV/20 mA; Cu Kα 1.54 Å).

For the sake of completeness the preparation of the catalyst and the THF homopolymer will be repeated here.

Preparation of the Catalyst. $P(CN)_3$ was prepared by adding 5 g of PCl_3 in 20 ml of CH_3CN (dried over P_2O_5 and distilled) to 15 g of AgCN vigorously stirred in 200 ml of CH_3CN under dry nitrogen. After 2 h at room temperature the product was filtered under nitrogen and the acetonitrile was removed on a rotary evaporator with a bath temperature of 318 K. When a solid residue was obtained, air was admitted and the flask was stoppered. On standing for 24 h the change from white to orange form occurred. This product was used in the polymerization studies.

Preparation of Polytetrahydrofuran. Previous to its use in the polymerization reaction THF (predried over KOH) was distilled from sodium and collected over molecular sieve. To 3.54 g (49.2 mmol) of THF 0.1 g of the above-mentioned catalyst was added and the mixture was shaken at room temperature. Within a few minutes the yellow color of the solution intensified and concomitantly the viscosity increased until the original solution solidified to a transparent yellow-brown solid after about 1 h. After standing for 2 days the reaction mixture was dissolved in 100 ml of THF and the polymer was precipitated as white rubbery solid by adding this solution dropwise to 1 L of ice water in a high-speed blender. Upon repetition of the dissolution and precipitation operations a white tough product, finally dried in the vacuum oven at 298 K for 48 h, was obtained with a yield of 49%. Anal. Calcd for C_4H_8O: C, 66.7; H, 11.1; O, 22.2. Found: C, 66.3; H, 11.2; O, 22.3. Intrinsic viscosity [η] in chlorobenzene, 75 mL/g.

Preparation of Poly-(ϵ-caprolactone). Catalyst (52 mg) was added to 2.76 g (24.2 mmol) of ϵ-caprolactone. The reaction mixture immediately took up a red color. At room temperature the viscosity increased only slowly but heating to 333 K overnight produced a very viscous solution. After dilution with 40 ml of THF the solution was added dropwise under vigorous stirring to 400 ml of H_2O when the

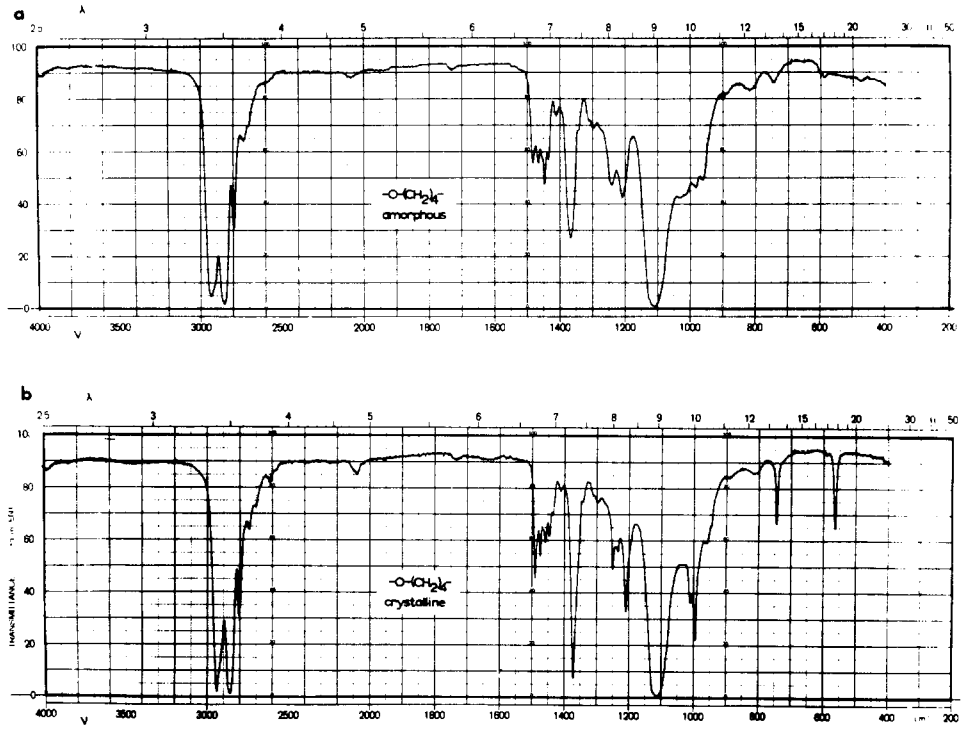

Figure 1. IR spectra of: (a) amorphous (323 K) poly(tetrahydrofuran); (b) crystalline (295 K) poly(tetrahydrofuran).

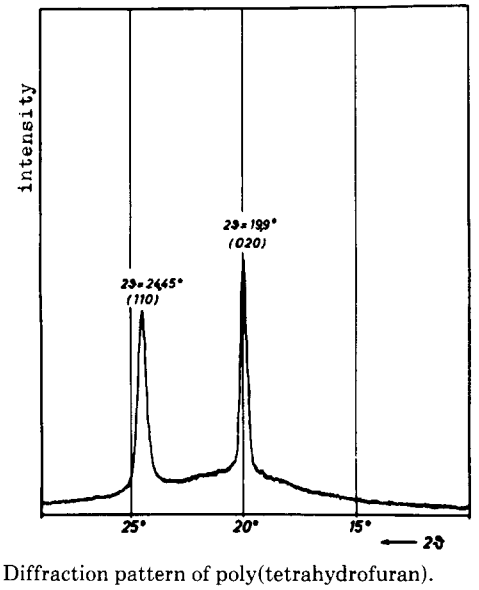

Figure 2. Diffraction pattern of poly(tetrahydrofuran).

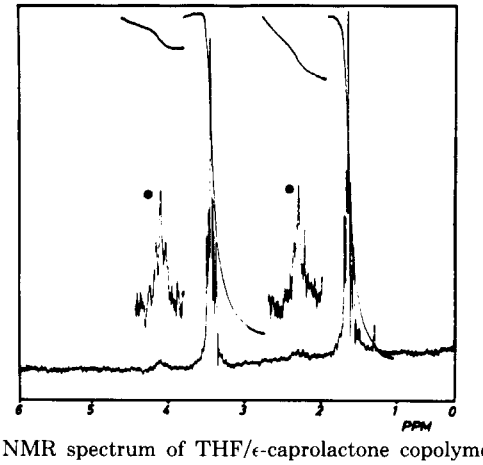

Figure 4. NMR spectrum of THF/ϵ-caprolactone copolymer (⊗ increased sensitivity).

polymer precipitated as white solid. The product was dissolved in THF and reprecipitation by the same procedure followed by drying under vacuum for 48 h at 308 K furnished a polymeric material in a yield of 50%. Intrinsic viscosity [η] in benzene, 18 mL/g. Anal. Calcd for $C_6H_{10}O_2$: C, 63.1; H, 8.8; O, 28.1. Found: C, 62.3; H, 8.5; O, 27.8; P, 0.7.

Copolymerization of THF and ϵ-Caprolactone. Catalyst (32 mg) was added to a mixture of 1.71 g (23.7 mmol) of predried THF and 459 mg (4.03 mmol) of ϵ-caprolactone and the solution was shaken at room temperature. After about 2 h the yellowish solution solidified. Upon standing overnight at room temperature the reaction mixture was

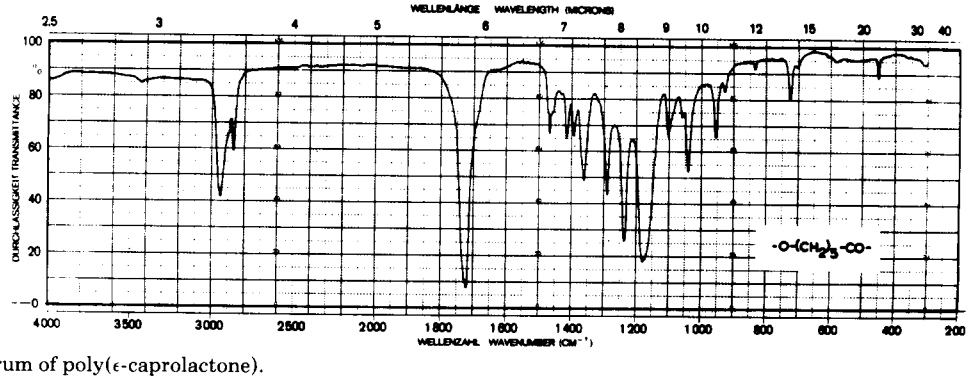

Figure 3. IR spectrum of poly(ϵ-caprolactone).

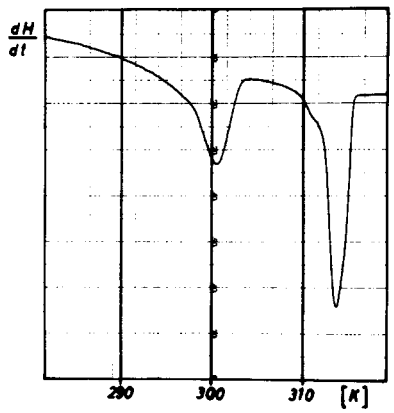

Figure 5. DSC diagram of THF/ϵ-caprolactone copolymer.

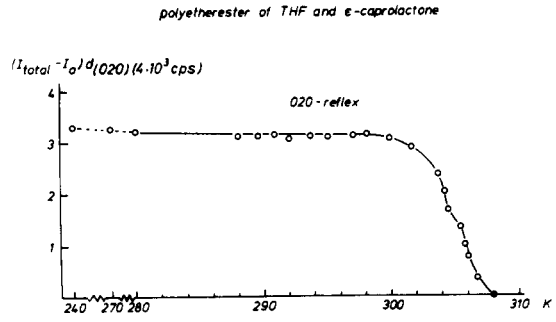

Figure 6. Temperature dependence of the 020 x-ray reflex intensity of the THF/ϵ-caprolactone copolymer.

dissolved in 40 ml of THF and this solution was added dropwise under vigorous stirring to 400 ml of ice water whereupon a white rubbery solid precipitated. The yield of purified (by repeated dissolution and precipitation) and dried (at 298 K for 48 h in the vacuum oven) product was 57%. Inherent viscosity η_{inh} (0.5% w/v in benzene), 33 mL/g. Anal. Found: C, 65.2; H, 10.6; O, 23.5; N, 0.5; P, 0.5.

Copolymerization of THF and γ-Butyrolactone. To the mixture of 3.69 g (51.2 mmol) of THF and 616 mg (7.16 mmol) of γ-butyrolactone 80 mg of catalyst was added. Solidification of the yellow reaction mixture occurred after about 1 h of shaking at room temperature. After standing at room temperature for 3 days the reaction mixture was dissolved in 100 ml of THF and a white rubbery solid was precipitated by dropwise addition of this solution to 1 L of vigorously stirred ice water. The purification and drying procedures were performed in analogy to the previous synthesis and the final product was obtained in an overall yield of 54%. Inherent viscosity η_{inh} (0.5% w/v in benzene), 67 mL/g. Anal. Found: C, 65.3; H, 10.8; O, 23.1; N, 0.5; P, 0.5.

Results and Discussion

Poly(tetrahydrofuran). From the intrinsic viscosity a molecular weight $\overline{M}_w$ of about 130 000 was derived.[13] The DSC diagram showed an endotherm at the crystalline melting point between 308 and 315 K with a melting enthalpy $\Delta H_m \approx 150$ J/g. The IR spectra (film from benzene on KBr) of the molten and recrystallized polymer are shown in Figure 1 and clearly reflect the spectroscopic changes upon recrystallization.[14] Adopting a monoclinic unit cell with the dimensions $a = 5.6$ Å, $b = 8.9$ Å, $c = 12.1$ Å, and $\beta = 134.1°$, the observed wide-angle x-ray reflexes (Figure 2) at $2\theta = 19.9°$ and $2\theta = 24.45°$ can be indexed as 020 and 110 reflexes, respectively.[15-17]

Poly(ϵ-caprolactone). The molecular weight $\overline{M}_w$ of the polymer evaluated with the measured intrinsic viscosity by the viscosity–molecular weight relationship[18]

$$[\eta] = 9.94 \times 10^{-5} \overline{M}_w^{0.82}$$

was about 10000. From the endothermic peak in the DSC diagram between 322 and 330 K a heat of fusion ΔH_m of 209 J/g was derived. The IR spectrum (on KBr pellet) of the crystalline polymer is shown in Figure 3. The observed wide-angle x-ray reflexes at $2\theta = 21.48°$ and $2\theta = 23.82°$ can be indexed as 110 and 200 reflexes on the basis of an orthorhombic unit cell[19] with dimensions $a = 7.5$ Å, $b = 5.0$ Å, and $c = 17.0$ Å.

Poly(ether ester) of THF and ϵ-Caprolactone. Clear solutions of the polymeric material in ether and ethyl acetate, in which the corresponding homopolymers are not soluble,

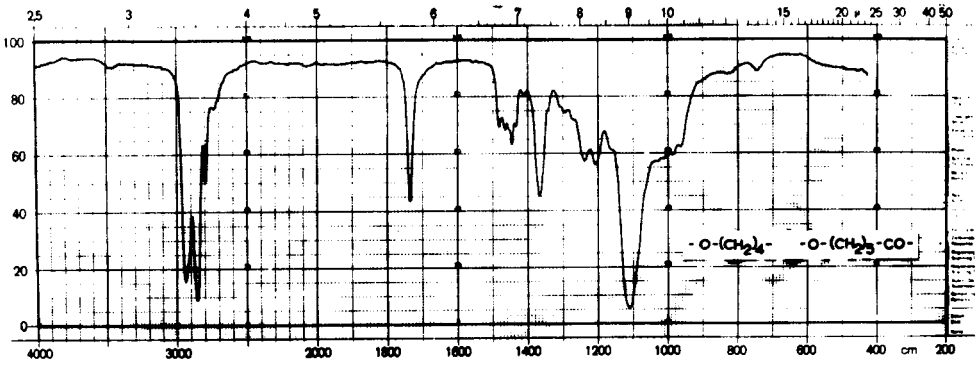

Figure 7. IR spectrum of THF/ϵ-caprolactone copolymer (323 K).

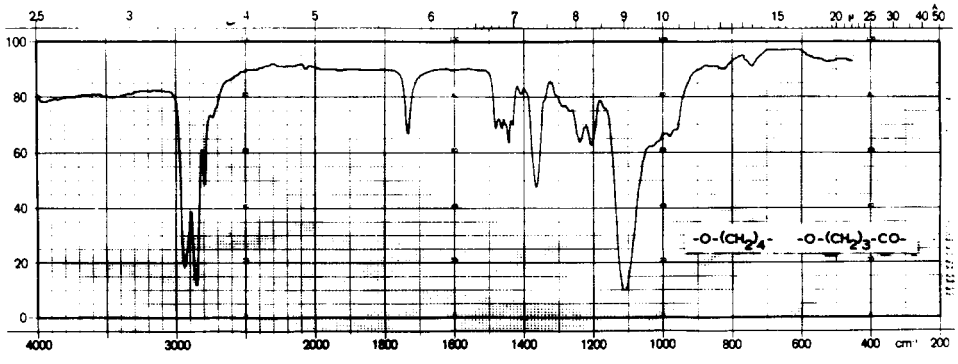

Figure 8. IR spectrum of THF/γ-butyrolactone copolymer (323 K).

indicate that copolymerization has taken place.[4] In the NMR spectrum (Figure 4) the two intense multiplets at 1.6 and 3.4 ppm can be assigned to the $-O-CH_2-\underline{CH_2}-\underline{CH_2}-CH_2-O-$ and $-O-CH_2-(\underline{CH_2})_3-CH_2-O-$ and to the $-\underline{CH_2}-\underline{CH_2}-O-\underline{CH_2}-CH_2-$ protons, respectively. From the intensity of the weak signals at 2.4 ppm ($-CH_2-CH_2-C(O)-O-$) and 4.1 ppm ($-CH_2-C(O)-O-\underline{CH_2}-CH_2-$) the content of ϵ-caprolactone units was estimated to about 5 mol %.

In the wide-angle x-ray diagram no reflexes were observed at the positions of the ϵ-caprolactone homopolymer but the somewhat broadened 020 and 110 reflexes at $2\theta = 19.65°$ and $2\theta = 24.15°$ indicate that the ϵ-caprolactone segments fit into the monoclinic unit cell of poly(tetrahydrofuran) with a concomitant widening of the lattice and decrease in crystallinity. The two endotherms observed in the DSC diagram (Figure 5) with maxima at 301 and 313 K can be attributed to the melting of crystalline, random, on alternating[20] copolymer segments (heat of fusion $\Delta H_m = 40$ J/g) and THF homopolymer segments (heat of fusion $\Delta H_m = 75$ J/g), respectively. This assumption is also confirmed by the shoulder observable in the intensity–temperature curve of the 020 x-ray reflex at 305 K (Figure 6). The IR spectrum (film from benzene on KBr plate) (Figure 7) of the molten copolymer (323 K) shows the ν(C=O) (1735 cm^{-1}) and ν(C–O–C) (small shoulder at 1165 cm^{-1}) stretching vibrations of the ϵ-caprolactone units superimposed on the poly(tetrahydrofuran) spectrum.

Poly(ether ester) of THF and γ-Butyrolactone. Here too, solubility of the polymer in ether and ethyl acetate in which the THF homopolymer is not soluble has been observed. In contrast to the previous copolymer, however, NMR spectroscopy indicates that γ-butyrolactone has been actually copolymerized in a lower proportion (<3%). This is also reflected in the IR spectrum of the copolymer by the weaker intensity of the ν(C=O) stretching vibration at 1735 cm^{-1} (Figure 8). The DSC diagram also shows two endothermic peaks at 301 and 321 K with heat of fusions $\Delta H_m \sim 9$ J/g and $\Delta H_m = 145$ J/g, respectively. Apart from the relatively low content of γ-butyrolactone steric considerations show that the ester units can be easier accomodated in the crystal lattice of the THF homopolymer and consequently the 020 and 110 wide-angle x-ray reflexes at $2\theta = 19.85°$ and $2\theta = 24.3°$ are less broadened than in the case of the ϵ-caprolactone copolymer. No significant break in the intensity–temperature curve of the 020 x-ray reflex could be observed for this copolymer.

We are currently testing the effectiveness of the catalytic system for other possible ring opening polymerizations. The results of these investigations and of systematic THF/ϵ-caprolactone and THF/γ-butyrolactone copolymerization experiments will be published later.

References and Notes

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A New Difunctional Anionic Initiator

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ABSTRACT: A new difunctional initiator for the preparation of 1,4-polyisoprene in hydrocarbon solvents has been obtained by the addition of *sec*-butyllithium to *m*-diisopropenylbenzene in the presence of 0.1 molecule of triethylamine per lithium site and subsequent reaction with 5 molecules of isoprene per lithium site. With this initiator, isoprene can be polymerized rapidly to an α,ω-dilithiopolyisoprene that has about the same microstructure as polymer obtained by initiation with a monoalkyllithium.

In one of several routes to ABA triblock copolymers from dienes and styrene, the diene is converted to an α,ω-dilithio-1,4-polydiene by initiation with a difunctional lithium carbanion followed by addition of styrene. This scheme has been employed by Fetters and Morton,[2] who used 1,4-dilithio-1,1,4,4-tetraphenylbutane to prepare the polydiene. The butane was obtained by reacting diphenylethylene with lithium in a hydrocarbon solvent containing a small amount of an aromatic ether. Later Karoly[3] described a similar scheme using 1,4-dilithio-1,4-dimethyl-1,4-diphenylbutane to make the polydiene. Karoly's butane was synthesized by reaction of α-methylstyrene with lithium in a hydrocarbon solvent using tetrahydrofuran as a promoter. In both dilithiobutane syntheses, the ether was necessary for the reaction. However, ether content was kept low enough to permit synthesis of polyisoprenes of relatively high cis-1,4 content.

Both compounds gradually lose solubility through association of alkyl lithiums, which leads to agglomerates of inactive