# Polylactones. 10. Cationic Polymerization of δ-Valerolactone by means of Alkylating Reagents

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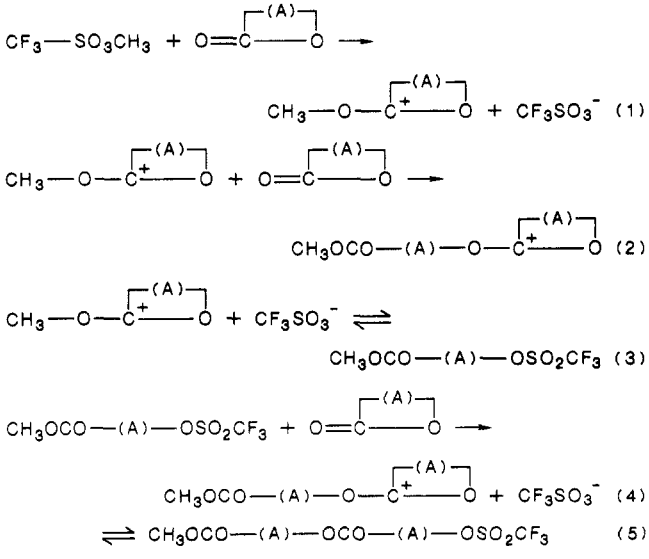
ABSTRACT: δ-Valerolactone was polymerized in nitrobenzene at 20 and 50 °C by means of methyl tosylate, methyl methanesulfonate, dimethyl sulfate, methyl triflate, ethyl fluorosulfate, and triethyloxonium fluoroborate. The best results with regard to both yields and polymerization rates were obtained with methyl triflate, the poorest results with methyl tosylate and methyl methanesulfonate. The highest yields were obtained at the lowest polymerization temperature, because degradation due to back-biting competes with polymerization. The formation of cyclic oligomers by degradation via back-biting was evidenced by GPC measurements. Because of competing degradation, yields near 100% were only obtained with high monomer/initiator ($M/I$) ratios (>200). With $M/I$ ratios of 400, weight-average molecular weights ($\bar{M}_w$) up to $50 \times 10^3$ and $\bar{M}_w/\bar{M}_n$ ratios near 2 were found. Methyl triflate initiated solution polymerizations in chloroform, 1,2-dichloroethane, nitrobenzene, and nitromethane revealed that the polarity of the solvent does not have a major influence on the rate of polymerization, indicating that formation and solvation of ionic species is not the rate-determining step. $^1$H NMR spectroscopic end-group analyses demonstrate that alkylating initiators yield poly(δ-valerolactone) with alkyl ester end groups. Therefore both initiation and propagation steps must involve cleavage of the alkyl–oxygen bond. Both IR and $^1$H NMR spectra show that methyl triflate exclusively methylates the exocyclic oxygen of δ-valerolactone. The resulting dioxocarbenium ion is less reactive than the covalent initiator, suggesting that the chain growth mainly proceeds via triflate ester end groups.

## Introduction

The cationic polymerization of lactones has recently attracted new interest, because the hitherto postulated polymerization mechanism[1-5] obviously deserves complete revision. In previous decades electrophilic attack at the endocyclic oxygen of a lactone followed by cleavage of the acyl–oxygen bond and chain growth via free acylium ions was believed to be an adequate formulation of cationic initiation and propagation. However, recent results obtained with β-propiolactone,[6,7] ε-caprolactone,[7] and L,L-lactide[8] clearly indicate that initiation and propagation involve alkylation of the exocyclic oxygen along with cleavage of the alkyl–oxygen bond (e.g., eq 1–4). Whereas



these two reaction steps seem to be of general validity for cationic polymerizations of all lactones, the reactivity and relative concentration of active end groups (e.g., cyclic dioxocarbenium ions) seem to vary largely with the nature of the lactone.[7] This aspect needs further investigation and was one of the objectives of the present work.

The cationic polymerization of lactones is also of preparative interest, because under appropriate conditions, the growing polylactones possess highly reactive, living chain ends. These living end groups may enable the synthesis of block copolyesters[9] and also the synthesis of more or less random copolyesters.[9-11] Furthermore, they may be responsible for rapid degradation of polylactones due to back-biting. The sensitivity of a lactone and its polyester to cationic transesterification and back-biting depends on nucleophilicity and basicity of the ester groups. Hence, the reaction conditions need careful optimization for preparative purposes. It was, thus, the second purpose of this work to study the preparative aspect of the cationic polymerization of δ-valerolactone.

## Experimental Section

**Materials.** δ-Valerolactone was purchased from Aldrich Chemical Co. (St. Louis, MO). It was distilled under nitrogen over oligomeric 2,4-tolylene diisocyanate and freshly powdered calcium hydride. The solvents used as reaction media were distilled over $P_4O_{10}$.

**Polymerizations of δ-Valerolactone (Tables I-III and Figure 1).** δ-Valerolactone (5.0 g, 50 mmol) was weighed under nitrogen into a 50-mL Erlenmeyer flask with ground-glass joints and silanized glass walls. A dry solvent (25 mL) and 0.5 mL of a 1 M solution of the initiator in chloroform (or dichloromethane) was added. The reaction vessel was closed with a glass stopper and steel spring and completely immersed into a thermostated oil bath. Finally the reaction mixture was diluted with 25 mL of dichloromethane and poured into 600 mL of ice-cold methanol. The precipitated poly(δ-valerolactone) was isolated by filtration, washed with methanol, and dried at 25–40 °C under a vacuum of ca. $10^{-1}$ mbar.

**$^1$H NMR Measurements.** A 2 M solution (0.5 mL) of a lactone and 0.6 mL of a 2 M solution of methyl triflate in $CDCl_3$ were mixed in a 5-mm-o.d. sample tube and stored at room temperature for 3 days. Afterward $^1$H NMR spectra were recorded with a Bruker AM 360 FT spectrometer.

**$^{13}$C NMR Measurements.** A 2 M solution (1 mL) of a lactone and 2 mL of a 2 M solution of methyl triflate in $CDCl_3$ were mixed in a 10-mm-o.d. sample tube and stored for 3 days at room temperature. Afterward, 20.2-MHz $^{13}$C NMR spectra were recorded on a Bruker WP 80 FT spectrometer with a pulse length of 45°,8K data points/5000-Hz spectral width, and a relaxation delay of 2 s.

**IR Spectra (Figures 2 and 3).** A lactone (10 mmol) and methyl triflate or ethyl fluorosulfate (20 mmol) were mixed in

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**Table I**
**Reaction Conditions and Yields of Polymerizations of δ-Valerolactone Initiated by Various Initiators**

| no. | initiator | $M/I$[a] | temp, °C | time, h | yield, %[b] series 1 | yield, %[b] series 2 | $\eta_{inh}$, dL/g |
|---|---|---|---|---|---|---|---|
| 1 | methyl tosylate | 100/1 | 20 | 96 | 0 | | |
| 2 | methyl tosylate | 100/1 | 50 | 96 | 1 | | |
| 3 | methyl methanesulfonate | 100/1 | 20 | 96 | 0 | | |
| 4 | methyl methanesulfonate | 100/1 | 50 | 96 | 1 | | |
| 5 | dimethyl sulfate | 100/1 | 20 | 24 | 9 | | 0.10 |
| 6 | dimethyl sulfate | 100/1 | 20 | 48 | 15 | | 0.17 |
| 7 | dimethyl sulfate | 100/1 | 20 | 96 | 49 | | 0.24 |
| 8 | dimethyl sulfate | 100/1 | 50 | 12 | | 3 | |
| 9 | dimethyl sulfate | 100/1 | 50 | 24 | 15 | 20 | 0.21 |
| 10 | dimethyl sulfate | 100/1 | 50 | 72 | 40 | 42 | 0.17 |
| 11 | dimethyl sulfate | 100/1 | 50 | 96 | 55 | 51 | 0.11 |
| 12 | ethyl fluorosulfate | 100/1 | 20 | 24 | 29 | | 0.28 |
| 13 | ethyl fluorosulfate | 100/1 | 20 | 48 | 46 | | 0.15 |
| 14 | ethyl fluorosulfate | 100/1 | 20 | 96 | 62 | | 0.15 |
| 15 | ethyl fluorosulfate | 100/1 | 50 | 12 | | 23 | |
| 16 | ethyl fluorosulfate | 100/1 | 50 | 24 | 51 | 43 | 0.30 |
| 17 | ethyl fluorosulfate | 100/1 | 50 | 72 | 68 | 63 | 0.14 |
| 18 | ethyl fluorosulfate | 100/1 | 50 | 96 | 74 | 69 | 0.10 |
| 19 | triethyloxonium tetrafluoroborate | 100/1 | 20 | 48 | 13 | 15 | 0.14 |
| 20 | triethyloxonium tetrafluoroborate | 100/1 | 20 | 96 | 37 | | 0.17 |
| 21 | triethyloxonium tetrafluoroborate | 100/1 | 50 | 48 | 60 | | 0.34 |
| 22 | triethyloxonium tetrafluoroborate | 100/1 | 50 | 96 | 71 | | 0.34 |

[a] Initial monomer/initiator ratio. [b] Two series of polymerizations were conducted with different batches of monomer and initiator.

a 10-mm-o.d. sample tube and stored at room temperature for 2 days. One drop of the reaction mixture was measured after 5 min, 30 min, 1 h, 2 h, 8 h, and 2 days between NaCl prisms with a Perkin-Elmer Model 257.

**Molecular Weight Measurements.** The inherent viscosities were measured with an automated Ubbelohde viscosimeter thermostated at 20 °C. A concentration of 2 g/L in dichloromethane was used in all cases. Weight-average molecular weights were determined by viscosity measurements in tetrahydrofuran at ca. 22 °C. The Staudinger indices were graphically evaluated, and the molecular weights were calculated by means of the Mark–Houwink equation of ref 12. Weight-average molecular weights ($\bar{M}_w$) were also determined by means of gel permeation chromatography in THF at ca. 25 °C. A Waters chromatograph Md 200 was used with a combination of four Ultrastyragel columns and was equipped with an IR detector. Commercially available polystyrene standards ($\bar{M}_w/\bar{M}_n < 1.1$) were used for the calibration, and by means of their Staudinger indices measured in THF a universal calibration curve was calculated. Number-average molecular weights ($\bar{M}_n$) were measured in chloroform by means of a Hitachi–Perkin-Elmer Model 117.

## Results and Discussion

**Optimization of Reaction Conditions.** Alkylating reagents were chosen as cationic initiators because they yield stable end groups (alkyl ester or alkyl ether groups, see discussion below) in contrast to protic acids or Lewis acids. These alkyl ester end groups have three characteristic advantages. First, they stabilize the chain end against degradation by transesterification in the form of a zip mechanism. Second, $^1H$ and $^{13}C$ NMR spectroscopic identification of end groups contributes substantially to the elucidation of the polymerization mechanism. Third, quantification of the $^1H$ NMR signal intensities may enable a calculation of the average degree of polymerization ($\overline{DP}$) provided the active chain end did not cause back-biting degradation. Because previous studies had shown that alkylsulfonates or sulfates, in particular methyl triflate, are good initiators and easy to handle, they were also preferentially used in the present work.

In order to optimize the reaction conditions with regard to yield, rate of polymerization, and molecular weight the following parameters were varied: initiator, reaction time, temperature, solvent, and monomer/initiator ratio ($M/I$). Tables I and II contain the results obtained with six different initiators in nitrobenzene. Methyl tosylate and methyl methanesulfonate are clearly not reactive enough to serve as initiators (no. 1–4, Table I). At 20 °C methyl triflate (Table II) is more effective than dimethyl sulfate, ethyl fluorosulfate, or triethyloxonium fluoroborate with respect to both yield and rate of polymerization.

**Table II**
**Methyl Triflate Initiated Polymerizations of δ-Valerolactone in Nitrobenzene at Various Temperatures ($M/I$ = 100)**

| no. | temp, °C | time, h | yield, %[a] series 1 | yield, %[a] series 2 | $\eta_{inh}$,[b] dL/g |
|---|---|---|---|---|---|
| 1 | 20 | 8 | 30 | | 0.14 |
| 2 | 20 | 18 | 63 | | 0.18 |
| 3 | 20 | 24 | 72 | 66 | 0.21 |
| 4 | 20 | 48 | 83 | 78 | 0.22 |
| 5 | 20 | 72 | 86 | | 0.24 |
| 6 | 20 | 96 | 88 | 90 | 0.24 |
| 7 | 50 | 8 | 0 | | 0.25 |
| 8 | 50 | 16 | 55 | | 0.28 |
| 9 | 50 | 24 | 65 | 67 | 0.26 |
| 10 | 50 | 48 | 67 | | 0.24 |
| 11 | 50 | 72 | 72 | 73 | 0.23 |
| 12 | 50 | 96 | 66 | 70 | 0.22 |
| 13 | 80 | 4 | 41 | | 0.18 |
| 14 | 80 | 8 | 42 | | 0.19 |
| 15 | 80 | 16 | 41 | | 0.18 |
| 16 | 80 | 24 | 33 | | 0.15 |
| 17 | 80 | 48 | 25 | | 0.14 |
| 18 | 80 | 72 | 6 | | 0.13 |

[a] Two series of polymerizations were conducted. [b] Measured at $c$ = 2 g/L in $CHCl_3$ at 20 °C; only polymers of the first series were measured.

Ethyl fluorosulfate and triethyloxonium fluoroborate gave similar yields as methyl triflate. Interestingly, the viscosities obtained with triethyloxonium fluoroborate (no. 21 and 22, Table I) are higher than those obtained with all other catalysts. This result is possibly the positive consequence of a less reactive chain end. As discussed below, both yields and molecular weights of cationically initiated poly(δ-valerolactone) strongly depend on the extent of degradation from the active chain end (back-biting). A less reactive chain end that can attack the cis ester bond of the monomer but not the trans ester groups

**Table III**
**Polymerizations of δ-Valerolactone by means of Methyl Triflate at Various $M/I$ Ratios in Nitrobenzene at 20 °C**

| no. | $M/I$[a] | time, h | yield, % | $\eta_{inh}$[b] | $\bar{M}_n$[c] (VPO) | $\bar{M}_n$[d] (calcd) | $\bar{M}_w$[e] (visc) | $\bar{M}_w$[f] (GPC) |
|---|---|---|---|---|---|---|---|---|
| 1 | 50 | 24 | 86 | 0.16 | 2.300 | 2.950 | 5700 | |
| 2 | 50 | 72 | 96 | 0.16 | | | 6600 | |
| 3 | 100 | 24 | 74 | 0.21 | 3.000 | 3.800 | | |
| 4 | 100 | 48 | 84 | 0.22 | | | | |
| 5 | 100 | 72 | 88 | 0.24 | 3.600 | 4.300 | 10000 | 13000 |
| 6 | 100 | 96 | 84 | 0.24 | | | | |
| 7 | 200 | 48 | 97 | 0.26 | 4.000 | 4.800 | 13000 | 17000 |
| 8 | 200 | 96 | 99 | 0.25 | | | | |
| 9 | 200 | 144 | 99 | 0.28 | 4.100 | 5.300 | 13500 | 20000 |
| 10 | 400 | 48 | 93 | 0.40 | 4.800 | 9.600 | 17500 | 28000 |
| 11 | 400 | 96 | 98 | 0.53 | | 15.000 | 22000 | 32000 |
| 12 | 400 | 144 | 100 | 0.65 | | 26.000 | 35000 | 47000 |

[a] Molar monomer/initiator ratio. [b] Measured with $c$ = 2 g/L in chloroform at 20 °C. [c] Vapor pressure osmometry in chloroform. [d] Calculated according to $\eta_{inh} = 0.48 \log M_n - 1.505$. [e] Determined by viscosity measurements from eq $[\eta] = (1.40 \times 10^{-4})M^{0.786}$ (THF, 25 °C, ref 12). [f] Gel permeation chromatography in THF.

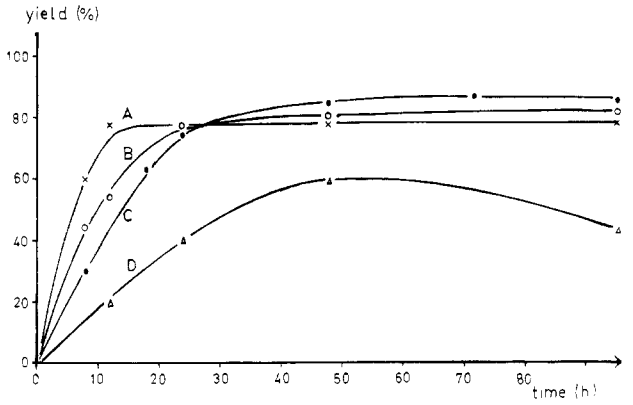


**Figure 1.** Time/conversion curves of methyl triflate initiated polymerizations of δ-valerolactone ($M/I$ = 100:1) in four different solvents at 20 °C: (A) in 1,2-dichloroethane; (B) in chloroform; (C) in nitrobenzene; (D) in nitromethane.

of the polymer is advantageous in this regard.

Variation of the reaction temperature with methyl triflate (Table II) demonstrates that the maximum yield decreases with increasing temperature. Variation of the reaction time reveals that both yield and viscosity pass through a maximum. These findings indicate that degradation, probably due to back-biting, competes with polymerization. If, as discussed below, the active chain end is a sulfate or sulfonate ester group, then its reactivity parallels that of the initiator. Thus, it is reasonable that the most effective initiator of this study, i.e., methyl triflate, is also most active in degradation. Similar results were obtained with ε-caprolactone; yet owing to the lower reactivity of monomer and poly(caprolactone) its optimum polymerization temperature is close to 50 °C when methyl triflate is used as initiator.[7] The influence of different solvents is evident from the data listed in Table IV and from Figure 1. With regard to yields and molecular weights, chloroform, 1,2-dichloroethane and nitrobenzene give similar results, whereas nitromethane is less favorable. However, the most interesting aspect is the rates of polymerization, which are higher in the less polar solvents 1,2-dichloroethane and chloroform. This surprising result suggests that the formation and stabilization of an ionic species is not (or not alone) the rate-determining step of the polymerization process.

When methyl triflate is used as initiator at various $M/I$ ratios, the highest yields were obtained with high $M/I$ ratios (Table III), provided the reaction time is sufficiently long. Viscosity measurements and vapor pressure osmometry agree in that high $M/I$ ratios and high yields are roughly paralleled by higher molecular weights. This

**Table IV**
**Polymerizations of δ-Valerolactone by means of Methyl Triflate ($M/I$ = 100) in Various Solvents at 20 °C**

| no. | solvent | DC[a] | time, h | yield, % | $\eta_{in}$[b] | $\bar{M}_n$[c] | $\bar{M}_w$[d] (visc.) |
|---|---|---|---|---|---|---|---|
| 1 | chloroform | 4.7 | 6 | 45 | 0.14 | 2600 | 6000 |
| 2 | chloroform | 4.7 | 12 | 51 | 0.17 | 3150 | 6800 |
| 3 | chloroform | 4.7 | 48 | 80 | 0.24 | 4300 | 10000 |
| 4 | chloroform | 4.7 | 96 | 82 | 0.26 | 4800 | 11000 |
| 5 | 1,2-dichloroethane | 10.4 | 6 | 80 | 0.14 | 2700 | |
| 6 | 1,2-dichloroethane | 10.4 | 12 | 78 | 0.18 | 3300 | 7300 |
| 7 | 1,2-dichloroethane | 10.4 | 48 | 76 | 0.21 | 3800 | 9000 |
| 8 | 1,2-dichloroethane | 10.4 | 96 | 76 | 0.21 | 3700 | |
| 9 | nitromethane | 38.6 | 12 | 19 | 0.14 | 2600 | 6000 |
| 10 | nitromethane | 38.6 | 48 | 59 | 0.21 | 3700 | |
| 11 | nitromethane | 38.6 | 96 | 42 | 0.19 | 3400 | 7500 |

[a] Dielectric constant determined at 25 °C. [b] Measured at $c$ = 2 g/L in $CHCl_3$ at 20 °C. [c] From vapor pressure osmometry in chloroform. [d] Determined by viscosity measurements from $[\eta] = (1.40 \times 10^{-4})\bar{M}_w^{0.786}$ (THF, 22 °C, ref 12).

finding in principle fits the so-called "living pattern" of anionic polymerization of vinyl monomers. However, an exact parallel of the $\overline{DP}$, $M/I$ ratio, and conversion is not expected for cationic polymerizations of lactones. First, transesterification and back-biting modify the original polymerization process in the direction of a thermodynamically controlled equilibrium of linear and cyclic oligo- or polyesters. Second, in the case of methyl triflate and ethyl fluorosulfate initiated polymerizations of δ-valerolactone, propagation is only slightly slower than initiation (see below). For the same reasons cationic polymerizations of δ-valerolactone are certainly not the optimum method for the preparation of high molecular weight poly(δ-valerolactone). In order to obtain some information on the absolute molecular weights of the samples listed in Tables III and IV, vapor pressure osmometry, viscosity measurements in combination with the Mark–Houwink equation $[\eta] = (1.40 \times 10^{-4})M_w^{0.786}$, and GPC measurements were conducted. The aforementioned Mark–Houwink equation was derived for poly(ε-caprolactone) on the basis of light-scattering measurements.[12] Nonetheless, the segmental mobility of poly(δ-valerolactone) should be nearly identical with that of poly(ε-caprolactone), so that this equation should also be useful for at least a crude characterization of poly(δ-valerolactone).

Vapor pressure osmometry gave number-average molecular weights ($\bar{M}_n$) in the range 2500–5000 for the samples listed in Table IV. These values may be 5–10% below the true $\bar{M}_n$'s because even a low content of solvent or unreacted δ-valerolactone, which is difficult to remove, may cause a significant depression of the molecular weights.

Nonetheless the observed order of magnitude is reasonable considering the $M/I$ ratio of 100, yields ≤82%, and the effect of back-biting. The inherent viscosities and $\bar{M}_n$'s of Table IV fit well to the equation $\eta_{inh} = 0.48 \log \bar{M}_n - 1.505$, which was used to check the consistency of the VPO measurements and to calculate the $\bar{M}_n$'s of the samples listed in Tables III. A comparison of the calculated and experimental values revealed that the latter are too low owing to the presence of nitrobenzene, which was also detected by $^1H$ NMR spectroscopy. Unfortunately intensive drying at 50 °C (0.01 mbar) did not enable complete removal of nitrobenzene, and substantially higher temperatures (above $T_m$) may cause degradation and distillation of δ-valerolactone.

When the $\bar{M}_w$ values resulting from viscosity measurements and the measured or calculated $\bar{M}_n$ values are compared, $\bar{M}_w/\bar{M}_n$ ratios in the range 1.4–2.0 are obtained. Considering that the rates of initiation and propagation are similar and considering the influence of back-biting, $\bar{M}_w/\bar{M}_n$ ratios below 2 are highly unlikely. However, since the $\bar{M}_w$ values were calculated from a Mark–Houwink equation determined for poly(ε-caprolactone), a better agreement may not be expected. Therefore GPC measurements were conducted in THF, and a universal calibration was established by means of polystyrene standards. The $\bar{M}_w$'s obtained in this way are higher (Table III) than those based on viscosity measurements and give $\bar{M}_w/\bar{M}_n$ ratios in the range 1.9–3.0, which is reasonable considering the influence of transesterification. Because the effect of back-biting must be greater for low $M/I$ ratios (at limited reaction time!) due to a higher concentration of active end groups, it is also reasonable that $\bar{M}_w/\bar{M}_n$ decreases with increasing $M/I$ ratio (Table III). Anyway, these measurements demonstrate that cationic polymerizations of δ-valerolactone may yield fairly high molecular weights when appropriate polymerization conditions are used.

**Chromatographic Analyses of Degradation Products.** When methyl triflate initiated polymerizations of δ-valerolactone are compared at different temperatures under variation of the reaction time, two interesting observations can be made. First, at 20 °C yields and molecular weights steadily increase with time (no. 1–6, Table II). Second, at 50 and 80 °C yields and molecular weights pass through a maximum with reaction time. Third, the negative trend of yields and molecular weights is more pronounced at 80 °C. All these results are best explained by the assumption that a degradation process involving the active chain ends competes with polymerization. Because every degradation of poly(δ-valerolactone) involves an attack on trans ester bonds, its energy of activation must be higher than that of the propagation step, so that the net effect of the degradation process is more pronounced at higher temperatures.

In order to obtain additional evidence for this degradation process, three series of methyl triflate initiated polymerizations were conducted in 1,2-dichloroethane, one series at 20 °C, one at 50 °C and one at 80 °C. After reaction times of 24, 48, 72, 96, 192, and 384 h samples of all three series were analyzed by means of GPC. For this purpose the solvent was removed by flash evaporation at 20–30 °C and the residual reaction mixture was analyzed without further treatment or fractionation. The polymerizations conducted at 20 °C did not show any degradation over the course of 14 days (Figure 2A). In contrast, the formation of oligomers was detectable at 50 °C even after 1 day, and their concentration slowly increased with time (Figure 2B). The degradation was still more pronounced at 80 °C (Figure 3). The fraction of cyclic oligomers and low molecular weight polymers steadily increased at the expense of the high molecular weight polyesters, and after 14 days the yield of poly(δ-valerolactone) insoluble in methanol had decreased to 45%. The degradation is faster in nitrobenzene as indicated by the results of Table II.

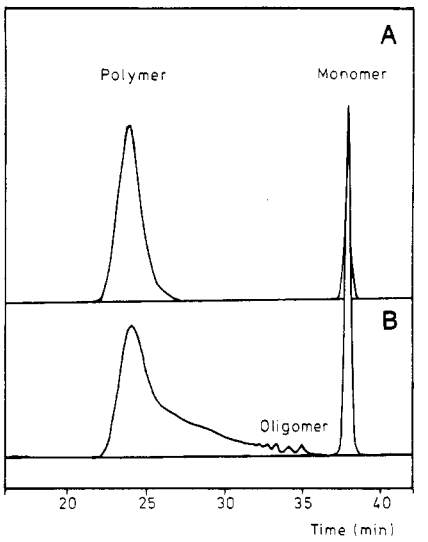


**Figure 2.** Gel chromatograms (the peak of 1,2-dichloroethane was eliminated) of methyl triflate initiated poly(δ-valerolactones): (A) reaction mixture after 7 days at 20 °C; (B) reaction mixture after 7 days at 50 °C.

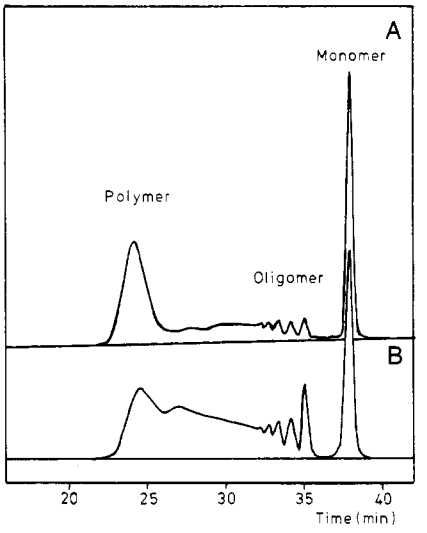


**Figure 3.** Gel chromatograms (the peak of 1,2-dichloroethane was eliminated) of methyl triflate initiated poly(δ-valerolactones): (A) reaction mixture after 1 day at 80 °C; (B) reaction mixture after 14 days at 80 °C.

The chromatograms of Figures 2 and 3 display at high retention times a continuous series of peaks representing the oligomeric degradation products. The individual members of this series were not identified by independent methods, yet a detailed investigation of this problem is in progress. Nevertheless, the set of Ultrastyragel columns used for this study was tested before by means of commercially available oligostyrenes and by means of oligostyrenes prepared by butyllithium-initiated polymerization at low $M/I$ ratios. These tests revealed that oligostyrenes up to the octamer give separate peaks. The monomer *n*-butylstyrene had the same retention time as δ-valerolactone, and the retention time of the dimer was similar to that of the first peak of the oligolactone series in Figures 2 and 3. Furthermore, a model of cyclodi-δ-valerolactone

demonstrated that the 12-membered ring can easily adopt two energetically favorable trans ester groups. Therefore, it is obvious that the series of oligomeric degradation products begins with the cyclodimer.

Finally, it is worth noting that on all three series of polymerizations a constant fraction of monomer was detectable (Figures 2 and 3). The incomplete conversion is obviously not a consequence of termination steps, because the degradation process indicates the presence of active chain ends. Thus, the presence of monomer in all reaction mixtures clearly originates from an unfavorable thermodynamic equilibrium of the polymerization. In other words, it indicates the well-known fact of a relatively low ceiling temperature of δ-valerolactone.

**IR Spectroscopic Investigation of the Polymerization Mechanism.** Cationic polymerizations of lactones initiated with alkylating reagents may yield polylactones with alkyl ester end groups, when exclusively the exocyclic oxygen is alkylated and chain growth proceeds via alkyl–oxygen bond cleavage (eq 1–4). $^1H$ and $^{13}C$ NMR end-group analyses enable an unambiguous identification of the end groups and thus a clear-cut decision whether initiation and propagation involve cleavage of the alkyl–oxygen or acyl–oxygen bond (see below). A question that cannot be answered by end-group analyses is the role of the equilibrium between the cyclic dioxocarbenium ion (**1**) and the corresponding covalent end group (**2**) (eq 3 and 5). In principle two different growing steps may occur. First the lactone reacts directly with the carbenium chain end **1** (eq 2). Second, the counterion reacts faster with the cyclic dioxocarbenium ion (eq 3), and the next growing step consists of a reaction between lactone and covalent chain end (eq 4).

The contribution that both propagation steps make to the overall chain growth depends on their reactivity (expressed by the rate constants in eq 6 and 7) and on their

$$V_2 = k_2[\mathrm{Pol^+CF_3SO_3^-}][\mathrm{lactone}] \quad (6)$$

$$V_4 = k_4[\mathrm{PolOSO_2CF_3}][\mathrm{lactone}] \quad (7)$$

$V_2$ and $V_4$ = polymerization rates of propagation for eq 2 and 4, respectively

$k_2$ and $k_4$ = rate constants of reactions 2 and 4, respectively

concentration. Although their reactivities are difficult to evaluate, it is, nonetheless, informative to determine the relative concentrations of both active chain ends, or in other words, the nature of the equilibria (3) and (5).

In order to suppress the chain growth and to increase the concentration of active species, δ-valerolactone was reacted with the double molar amount of methyl triflate, and IR spectra were recorded after 5 min, 2 h, 4 h, 1 day, and 2 days. As demonstrated in Figure 4 the carbonyl band of δ-valerolactone (1750 $cm^{-1}$) decreases in intensity until, after ca. 4 h, the thermodynamically stable equilibrium is reached. On the other hand, a new band appears at 1570 $cm^{-1}$ and increases in intensity at the same time. This spectroscopic result indicates the formation of a cyclic dioxocarbenium ion according to eq 1, because only this reaction product may show a new band at significantly lower wavenumbers. For the covalent triflate resulting from ring opening (eq 3) the typical carbonyl band of a linear ester is expected at ca. 1740 $cm^{-1}$. Methylation at the endocyclic oxygen (eq 8) shifts the carbonyl band to even higher wavenumbers. When more δ-valerolactone is added to a 1-day-old 1:1 reaction mixture of δ-valerolactone and methyl triflate, the band at 1570 $cm^{-1}$ does not disappear, while the increasing viscosity of the reaction mixture indicates ongoing polymerization. However, when an equimolar solution of triphenylphosphine in chloroform is added, the band at 1570 $cm^{-1}$ disappears immediately, indicating that it originates from a species with high alkylating power. Thus these IR spectroscopic results along with the $^1H$ NMR spectra discussed below demonstrate that the equilibria of eq 1 and 3 both lay on the side of the cyclic dioxocarbenium ion, when methyl triflate is the initiator.

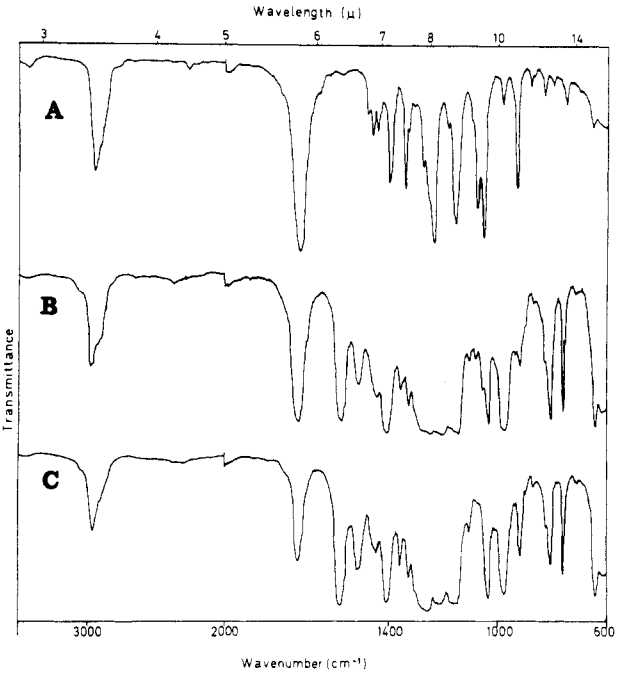


**Figure 4.** IR spectra of (A) δ-valerolactone, (B) reaction mixture of δ-valerolactone and methyl triflate (molar ratio 1:2) after 5 min, and (C) the same reaction mixture after 2 days.

Analogous IR spectroscopic studies were conducted with 1:2 reaction mixtures of δ-valerolactone and methyl methanesulfonate, dimethyl sulfate, and ethyl fluorosulfate. In the case of ethyl fluorosulfate the IR spectra were similar to those obtained with methyl triflate (Figure 5B,C). A new band at 1570 $cm^{-1}$ appeared, whereas the CO band at 1750 $cm^{-1}$ lost intensity. The reaction rate was slightly lower; yet the final equilibrium between lactone and its *O*-ethyl dioxocarbenium ion was similar to that obtained with methyl triflate. In analogy with polymerizations conducted with ε-caprolactone,[7] we must conclude that the lower yields obtained with ethyl fluorosulfate do not result from lower reactivity of this initiator.

When methyl methanesulfonate was used, no spectroscopic change was detectable even after 2 days (Figure 3A). Again no significant spectroscopic change was observed for dimethyl sulfate. However, the reaction mixture turned viscous and partially solidified in the course of 4 days, indicating that polymerization took place. Obviously a small fraction of the initiator reacted with the monomer. The question of why in this case propagation is faster than initiation is discussed below.

Finally it is noteworthy that a similar study was recently reported for mixtures of methyl triflate and ε-caprolactone.[7] In this case the cyclic dioxocarbenium ion was not detectable by means of IR spectroscopy and $^1H$ NMR spectra proved that the equilibrium of eq 3 lies far on the side of the covalent triflate. Obviously, the greater ring size favors ring opening of the cyclic dioxocarbenium ion. In contrast, methylation of γ-valerolactone yields a rather stable five-membered dioxocarbenium ion as demonstrated

**Table V**
**$^1$H NMR Chemical Shifts δ (ppm) of δ-Valerolactone and Its Derivatives Determined in Deuteriated Chloroform or Nitrobenzene Relative to Internal $Me_4Si$**

| compound | solvent | chemical shifts, δ | | | | |
|---|---|---|---|---|---|---|
| | | $H_\alpha$ | $H_\beta$ | $H_\gamma$ | $H_\delta$ | $OCH_3$ |
| δ-valerolactone | $CDCl_3$ | 2.55 (t) | 1.81 (m) | 1.87 (m) | 4.35 (t) | |
| *O*-methyl δ-valerolactone triflate | $CDCl_3$ | 3.07 (t) | 2.11 (m) | 2.17 (m) | 5.16 (t) | 4.33 (s) |
| triflate of δ-hydroxyvaleric acid methyl ester | $CDCl_3$ | 2.35 (t) | 1.77 (m) | 1.92 (m) | 4.72 (t) | 3.68 (s) |
| poly(δ-valerolactone) | $CDCl_3$ | 2.34 (t) | 1.68 (m) | 1.68 (m) | 4.08 (t) | 3.68 (s) |
| δ-valerolactone | $C_6D_5NO_2$ | 2.60 (t) | 1.83 (m) | 1.87 (m) | 4.36 (t) | |
| *O*-methyl δ-valerolactone triflate | $C_6D_5NO_2$ | 3.12 (t) | 2.11 (m) | 2.19 (m) | 4.21 (t) | 4.50 |
| poly(δ-valerolactone) | $C_6D_5NO_2$ | 2.39 (s)[a] | 1.74 (s)[a] | 1.75 (s)[a] | 4.16 (s)[a] | |

[a] Broad signals.

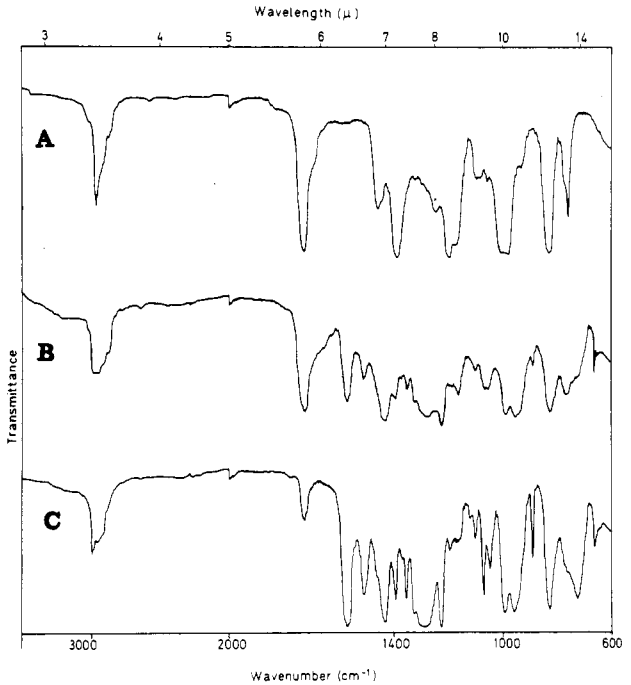


**Figure 5.** IR spectra of the following reaction mixtures: (A) δ-valerolactone + methyl methanesulfonate (molar ratio 1:2) after 2 days; (B) δ-valerolactone + ethyl fluorosulfate (molar ratio 1:2) after 5 min; (C) the mixture of (B) after 2 days.

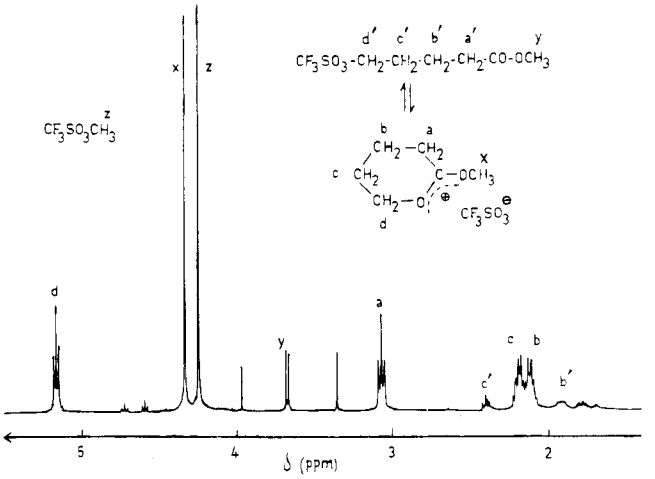


**Figure 6.** $^1$H NMR spectrum, 360 MHz, of the reaction mixture of δ-valerolactone and methyl triflate (molar ratio 2:1) measured in $CDCl_3$ after 2 days.

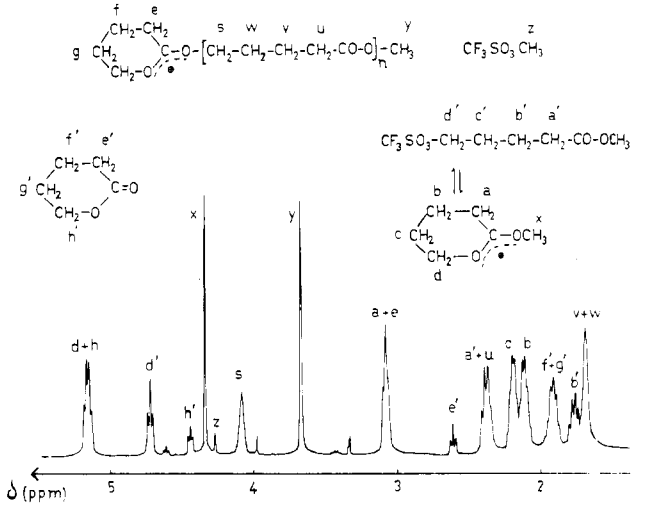


**Figure 7.** $^1$H NMR spectrum, 360 MHz, of the reaction mixture of δ-valerolactone and methyl triflate (molar ratio 2:1) measured in $CDCl_3$ after 2 days.

in a previous part of this series.[8] It is certainly a reasonable result that the thermodynamic stability of cyclic dioxocarbenium ions decreases in the order γ-lactone > δ-lactone > ε-lactone. Unfortunately, rapid polymerization prevented the observation of active species in the case of β-propiolactone/methyl triflate.[7]

**$^1$H and $^{13}$C NMR Spectroscopic Studies.** Various poly(δ-valerolactones) isolated from the experiments listed in Tables I–IV, were subjected to $^1$H and $^{13}$C NMR measurements in $CDCl_3$. Comparison of the chemical shifts with those of model compounds[15] revealed that in all cases methyl or ethyl ester end groups were formed and never ether end groups (Figure 7). Hence, the cationic polymerizations of δ-valerolactone proceed according to eq 1–5 involving cleavage of the alkyl–oxygen bond in perfect agreement with recent results obtained for β-propiolactone and ε-caprolactone.[7]

In order to obtain more information on the initiation step, in particular on the equilibria of eq 1 and 3, δ-valerolactone was reacted with methyl triflate at molar ratios of 1:2, 1:1, 2:1, and 5:1 and 360-MHz $^1$H NMR spectra of the reaction mixtures were measured in $CDCl_3$ after 3 days. From high-resolution $^1$H NMR spectra a clear-cut differentiation between free lactone, its *O*-methyl dioxocarbenium ion I, and the noncyclic triflate ester (II) is expected. Compared to the lactone the cyclic dioxocarbenium ion 1 should exhibit a $CH_3$ singlet (x in Figures 6 and 7) downfield of methyl triflate (z in Figures 6 and 7). Furthermore, both α-$CH_2$ and δ-$CH_2$ signals (a and d) must show a considerable downfield shift relative to those of the free lactone (e′ and h′ in Figure 7). In contrast a normal methyl ester singlet (ca. 3.7 ppm) is expected for the linear triflate ester (y in Figure 7) and a weaker downfield shift of the O–$CH_2$ signal (d′), because the deshielding effect of the triflate group is weaker than that of the positive charge. Furthermore, only negligible downfield shhift is expected for the α-$CH_2$ signal (a′) in the linear triflate II. The $^1$H NMR chemical shifts of all

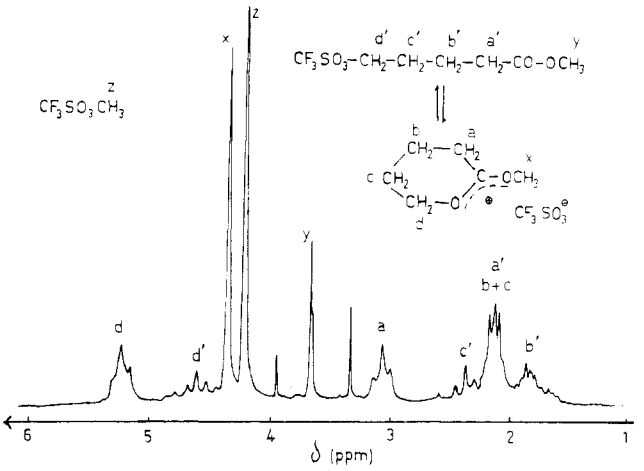


**Figure 8.** $^1H$ NMR spectrum, 80 MHz, of the reaction mixture of δ-valerolactone and methyl triflate (molar ratio 1:2) measured after 2 days in $CDCl_3$ (identical with that of Figure 6).

clearly identified species along with those of poly(δ-valerolactone) are listed in Table V. The $^1H$ NMR spectra recorded with $CDCl_3$ as reaction medium clearly demonstrate that (a) the alkylation equilibrium 1 is shifted far to the right side and (b) that equilibrium 3 favors the cyclic dioxocarbenium ion I. Thus, at $M/I$ ratios of 1:2 or 1:1 the O-methylated lactone I is the main product in the reaction mixture (Figure 6), and the NMR spectroscopic results perfectly agree with those of IR spectroscopy (Figure 4). When the $M/I$ ratio increases, the signals of the monomeric unit gradually gain in intensity (signals u, v, w, and s in Figure 7). The most interesting observation concerns the equilibria of eq 3 and 5. At an $M/I$ ratio of 1:2 (Figure 6) equilibrium 3 is on the order of 8:1 in favor of the dioxocarbenium ion I, whereas it is only around 2:1 at $M/I$ ratios >2:1 (Figure 7). Because unreacted methyl triflate is present at the $M/I$ ratio of 1:2, the higher dielectric constant of the reaction medium possibly stabilizes the dioxocarbenium ion I at the expense of the covalent triflate 2. This hypothesis is supported by $^1H$ NMR measurements in deuteriated nitrobenzene and nitromethane. In both highly polar solvents the covalent triflate II is never detectable and the dioxocarbenium ion I seems to be the sole reaction product at a $M/I$ ratio of 1:2.

When the δ-valerolactone/methyl triflate mixture in $CDCl_3$ was measured at 80 MHz, relatively broad signals were found (Figure 8). This greater line width is neither the result of the lower field strength nor of a poorer field homogeneity, because the spectra of the pure lactone measured at nearly the same time under identical conditions displayed the expected good resolution. Furthermore, the signals sharpened when the temperature was raised or when the sample was measured at higher field strengths (Figure 6). These observations suggest that a slow exchange reaction is responsible for the line broadening observed at 80 MHz and 20 °C. Because alkylation equilibrium 1 is far from unity, the equilibration according to eq 3 is probably the origin of this exchange reaction. Anyway, with increasing temperatures the signals a'–d' gain in intensity, and because ring-opening is favored by entropy at higher temperatures, these signals were attributed to the triflate II. Both the IR and NMR spectroscopic measurements agree in that the dioxocarbenium ion I is the main reaction product of the initiation step. This result allows the important conclusion that the covalent initiator is significantly more reactive (i.e., electrophilic) than dioxocarbenium ion I. If this is likewise true for the covalent triflate end groups (e.g., II), the chain growth mainly proceeds by reaction of lactones with covalent triflate end groups, i.e., according to eq 3–5. In this connection it is noteworthy that the ring–chain equilibrium of methylated ε-caprolactone is shifted to the right side, i.e., to the covalent triflate.[7] This difference compared to δ-valerolactone is obviously a consequence of the greater ring size which favors ring opening for thermodynamic reasons. Also this observation fits well to a polymerization mechanism involving covalent triflate end groups.

## Conclusion

To the best of our knowledge the present results provide for the first time direct spectroscopic evidence for the intermediate formation of cyclic dioxocarbenium ions in the cationic polymerization of lactones. These spectroscopic results definitely prove that initiation and propagation involve alkylation of the exocyclic oxygen followed by cleavage of the alkyl–oxygen bond. The formation of dioxocarbenium ions as main product indicates that this ionic species may be less reactive than covalent triflate ester end groups, so that each propagation step involves alkylation of a lactone by a triflate end group (eq 3–5). If the chain growth proceeds via covalent triflate end groups, reaction of the cyclic dioxocarbenium ion with its counterion is a necessary reaction step which is favored by a low dielectric constant of the reaction medium. It fits well to this two-step propagation mechanism that the rates of polymerization in less polar solvents (chloroform, 1,2-dichloroethane) are as high or higher than those in highly polar solvents (nitrobenzene, nitromethane). The two-step propagation mechanism (eq 3–5) is further confirmed by the isolation of optically pure poly(L-lactide) from methyl triflate initiated polymerizations of L,L-lactide. Only two reactions steps, both involving Walden inversion, can account for 100% optical activity, when the ring cleavage involves the alkyl–oxygen bond.[8] Thus, it must be finally concluded that cationic polymerization of lactones may proceed via covalent end groups, which are more reactive than the isomeric ionic species. This conclusion is of particular importance because for nearly all ionic polymerizations of vinyl compound or cyclic monomers the ionic form of active chain ends is considered to be the most active species, whereas the covalent form is called a dead or dormant end group.

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**Registry No.** Poly(δ-valerolactone) (SRU), 26499-05-8; poly(δ-valerolactone) (homopolymer), 26354-94-9; methyl tosylate, 80-48-8; methyl methanesulfonate, 66-27-3; dimethyl sulfate, 77-78-1; ethyl fluorosulfate, 371-69-7; triethyloxonium tetrafluoroborate, 368-39-8; methyl triflate, 333-27-7; δ-valerolactone, 542-28-9.

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# Polymerization in Nonaqueous Lyotropic Liquid Crystals with a Polymerizable Solvent

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ABSTRACT: Lamellar liquid crystals of lecithin and 2-hydroxyethyl methacrylate (HEMA) were polymerized by using UV radiation. Optical microscopy, infrared spectroscopy, and small-angle X-ray diffraction were used to compare the structure prior to and after polymerization. The lamellar structure was retained after polymerization with increased interlayer spacing.

## Introduction

The properties of lyotropic liquid crystals based on surfactants have been extensively investigated[1-3] following the pioneering contributions by Ekwall.[4] In parallel with these investigations, a great volume of research has been reported on systems with lecithin and water,[5] an expected consequence of the importance of this combination for the structure of biological membranes.[6] Recently, the structure[6-10] as well as the dynamics[11] have been clarified of nonaqueous liquid crystals with lecithin as the amphiphile and various polar organic compounds as the solvent. These nonaqueous liquid crystals also have an importance for biological systems.[12]

The introduction of polymers into lamellar liquid crystals is a fascinating phenomenon of pronounced importance in understanding biological structures in which polysaccharides and proteins interact with the bimolecular organization of lecithin in the biomembrane.[13-17] Attempts to bring polymers into lamellar liquid crystals have met with limited succes[18] due to the space demands from the conformational freedom requirements of a high molecular weight polymer and the limited dimensions of a lamellar liquid crystal. Poly(ethylene glycol) of medium molecular weight has been included in lamellar liquid crystals.[19-22] Poly(ethylene glycol) of small molecular weight has been used as the sole solvent for lamellar liquid crystals with lecithin,[23] and polyacrylic acid of low molecular weight has been polymerized while retaining a thermodynamically stable lamellar liquid-crystalline structure.[24] Polymeric substances per se form liquid crystals[25-27] and the phase behavior of those with lyotropic side-chain polymers in aqueous solutions has been investigated.[28]

With this background, it appeared reasonable to approach the problem from the opposite angle to the earlier attempts of introducing a polymer into a liquid-crystalline phase based on water as the solvent. We found an approach using a polymerizable polar liquid as the solvent, a logical step in this area against the foundation of known structures of nonaqueous liquid crystals.[6-11] The present publication describes the polymerization of 2-(hydroxyethyl methacrylate) (HEMA) in a lamellar liquid crystal with lecithin.

## Experimental Section

**Materials.** The lecithin, L-α-phosphatidylcholine, was obtained from Sigma Chemical Co., No. P-3644, and hydroxyethyl methacrylate (HEMA) was supplied by Scientific Polymer Product. Disposable chromatographic columns DMR-4 from Scientific Polymer Product were used to remove the inhibitor and any polymer residue.

**Determination of the Lamellar Liquid-Crystalline Phase.** HEMA (30 wt %) was added to lecithin (70 wt %) by using small glass vials with screw tops. The sample was matured at 35 °C for at least 24 h by using a Blue M transite oven, and a vortex vibromixer was used every 2 h to facilitate vigorous mixing. Finally, the sample was left to equilibrate overnight at room temperature. The lamellar liquid crystals were confirmed by their optical pattern in polarized light in an optical microscope.

**Polymerization.** The polymerization was accomplished by UV radiation from an Ace Glass, 450-W quartz mercury arc lamp source. One hour was required for polymerization in the absence of initiator.

To remove the exothermic heat caused by polymerization, air was circulated through the reaction chamber covered with aluminum foil to maximize refraction of UV radiation.

**Optical Microscopy.** A small amount of the sample was deposited between a glass plate and cover slide to form a thin film. Polymerization was performed directly on this sample to compare the structure prior to and after polymerization. An Olympus microscope with crossed polarizers was used.

**X-ray Diffraction.** A small amount of equilibrated sample was drawn into a fine glass capillary tube, and polymerization was carried out in the tube (0.7-mm diameter). Wide-angle X-ray photographs were taken with GE Model 11, Ni-filtered Cu Kα radiation, with Debye-Scherrer camera.

**Infrared Spectroscopy.** A small amount of equilibrated sample was deposited between sodium chloride mediums to form a film of between 0.01- and 0.02-mm thickness. Polymerization was made in the sodium chloride cell and the spectra were recorded on a Perkin-Elmer 521 allgrating IR spectrophotometer.

## Results

The observed optical microscopic textures of lyotropic mesophases (Figure 1) formed by lecithin and HEMA, prior to an after polymerization, were characteristic of a lamellar liquid crystal. The typical "oily streaks" are present in both photos and the overall pattern is strikingly similar.

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