Eur. Polym. J. Vol. 24, No. 2, pp. 145–150, 1988
Printed in Great Britain

0014-3057/88 $3.00 + 0.00
Pergamon Journals Ltd

POLYLACTONES—14.* POLYMERIZATION OF δ-VALEROLACTONE AND ϵ-CAPROLACTONE BY MEANS OF TRIMETHYLSILYL TRIFLATE

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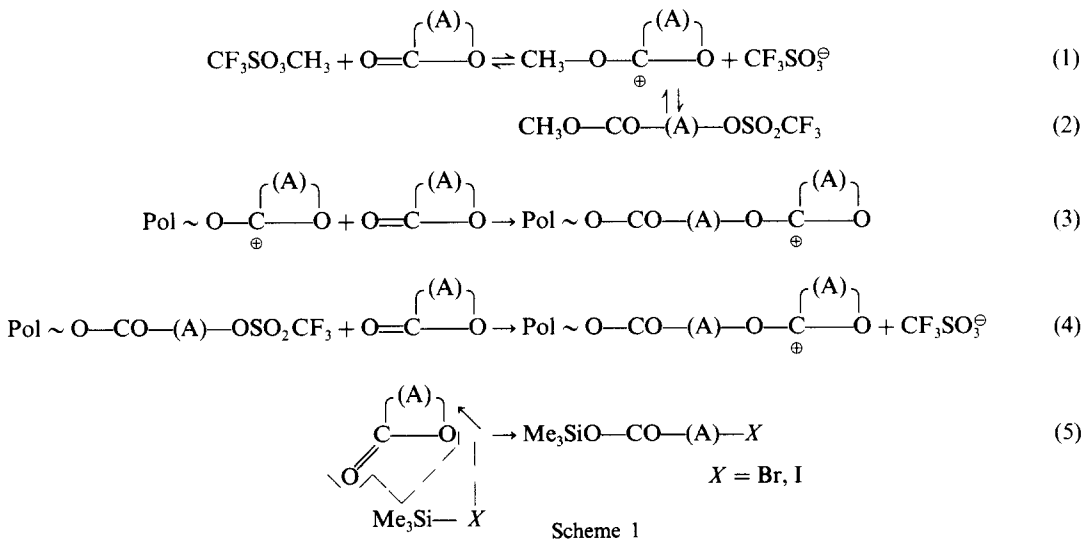
(*Received* 26 *March* 1987)

Abstract—Attempts were made to polymerize δ-valerolactone and ϵ-caprolactone with bistrimethylsilyl sulphate and trimethylsilyl (TMS) triflate in 1,2-dichloroethane or nitrobenzene but bistrimethylsilyl sulfate turned out to be inactive. Moderate yields (up to 65%) of poly(δ-valerolactone) and high yields (up to 96%) of poly(ϵ-caprolactone) were obtained with TMS-triflate, with weight average molecular weights ($\bar{M}_w$) up to 65,000 when high monomer/initiator ratios and long reaction times (8d) were used. The polymerization mechanism was investigated by means of i.r.- and ^{1}H-NMR spectroscopy. TMS-triflate does not react with γ-butyrolactone in contrast to methyltriflate which methylates the lactones. In the case of δ-valerolactone or ϵ-caprolactone, initiation with TMS-triflate is significantly slower than propagation. The active chain ends and the mode of ring-opening are the same as those for methyltriflate, but the reactivity of TMS-triflate is lower than that of methyltriflate or triflic acid, and its reaction with lactones is quite different from that of TMS-bromide and TMS-iodide.

INTRODUCTION

It has been demonstrated [1–4] that methyltriflate and triflic acid are highly effective initiators of the cationic polymerization of most lactones. The polymerization mechanism was elucidated by means of i.r.-, ^{1}H- and ^{13}C-NMR spectroscopy. The initiation step consists in methylation (or protonation) of the exocylic oxygen (Eqn 1) followed by partial ring opening of the activated lactone by its counterion (Eqn 2). The propagation consists of a reaction between lactone and cyclic dioxocarbenium ion (Eqn 3) or between lactone and triflate ester group (Eqn 4). Even though it is not clear which growing step is predominant, several arguments in favour of Eqn (4) were presented [3, 4].

When lactones are treated with chloro-, bromo- or iodotrimethylsilane at temperatures $\leqslant 80°C$, no reaction is detectable with TMS-Cl whereas TMS-Br and TMS-I react with the lactones almost quantitatively [5]. In analogy to methyltriflate, these silanes exclusively cleave the alkyl–O bond (Eqn 5); this cleavage is not followed by polymerization, because bromide and iodide are better nucleophiles and poorer leaving groups than triflate or fluorosulphate anions. Because lactones do not react with methylbromide or iodide, the high reactivity of TMS-Br and TMS-I must be attributed to the silyl group which can easily react with nucleophiles owing to its free d-orbitals. This



Scheme 1

*Part 13. H. R. Kricheldorf and I. Kreiser. *J. Macromolec. Sci.* In press.

conclusion suggests that TMS-triflate or bis-TMS-sulphate may be more reactive initiators than methyltriflate or dimethyl sulphate. This suggestion was supported by a recent short communication [6] claiming that TMS-triflate is a powerful initiator of vinyl ethers and cyclic ethers. Thus, it was obviously necessary to investigate the reactivity of TMS-triflate with lactones.

EXPERIMENTAL

Materials

TM-triflate and bis-TMS-sulphate were purchased from Aldrich & Co. (St. Louis, U.S.A.) and used without further purification. δ-Valerolactone and ϵ-caprolactone were also purchased from Aldrich & Co. and purified by distillation under N_2 over oligomeric 4,4′-diisocyanato diphenylmethane. 1,2-Dichloroethane was distilled over P_4O_{10}.

Polymerizations (Tables 1–3)

50 mmol of lactone and 25 ml of dry solvent were mixed in a 50 ml Erlenmeyer flask with silanized glass walls and a ground glass joint. The initiator was added in the form of a 1 M solution in 1,2-dichloroethane and the reaction vessel was closed with a glass stopper. The reaction mixture was stored in a thermostated oil-bath; the reaction product was then dissolved in dichloromethane and precipitated into cold methanol. Finally the precipitated polylactones were isolated by filtration and dried at 40°C/12 mbar. The preparation of the reaction mixture was conducted in a glove-box under an atmosphere of N_2 dried with P_4O_{10}.

Table 3. Methyltriflate-initiated polymerization of ϵ-caprolactone in 1,2-dichloroethane at 50°C

No.	M/I	Time (hr)	Yield (%)	η_{inh}* (dl/g)	$\bar{M}_w$†
1	50/1	24	85	0.20	—
2	50/1	48	89	0.22	—
3	50/1	96	89	0.23	13,000
4	100/1	48	88	0.27	—
5	100/1	96	92	—	—
6	100/1	120	96	0.40	25,000
7	200/1	96	85	0.44	—
8	200/1	192	97	0.55	32,000
9	400/1	96	76	—	—
10	400/1	192	93	0.78	58,000

*Measured with $c = 2$ g/l in dichloromethane at 25°C.
†Determined by GPC.

^1H-NMR spectroscopy

1 mmol TMS-triflate was weighed into a 5 mm o.d. sample tube and a solution of 0.5 mmol lactone in 0.6 ml $CDCl_3$ containing 1% TMS was added. The sample tube was sealed and examined in a Bruker AC-100 FF spectrometer after increasing time intervals.

i.r.-Spectroscopy

2 mmol TMS-triflate was weighed into a 10 mm o.d. sample tube and 1 mmol of a lactone was added without solvent. At intervals, one drop of this reaction mixture was spread between NaCl prisms and measured immediately with a Perkin–Elmer Md 257 i.r. spectrometer. Preparation and handling of the reaction mixtures for both i.r. and

Table 1. Polymerization of ϵ-caprolactone with TMS-triflate and bis-TMS-sulphate in 1,2-dichloroethane

No.	Initiator	M/I*	Temperature (°C)	Time (hr)	Yield (%)	η_{inh}†
1	bis-TMS-sulphate	50:1	20	48	0	—
2	bis-TMS-sulphate	50:1	20	96	0	—
3	bis-TMS-sulphate	100:1	50	48	0	—
4	bis-TMS-sulphate	100:1	50	96	0	—
5	bis-TMS-sulphate	100:1	80	48	0	—
6	bis-TMS-sulphate	100:1	80	96	0	—
7	TMS-triflate	100:1	20	48	1	—
8	TMS-triflate	100:1	20	96	10	0.20
9	TMS-triflate	100:1	50	48	70	0.28
10	TMS-triflate	100:1	50	96	89	0.38

*Initial monomer/initiator ratio.
†Measured with $c = 2$ g/l in dichloromethane at 25°C.

Table 2. TMS-triflate initiated polymerizations of ϵ-caprolactone in 1,2-dichloroethane at 50°C

No.	M/I*	Time (hr)	Yield (%)	η_{inh}† (dl/g)	$\bar{M}_w$‡	$\bar{M}_w$§
1	50	48	75	0.26	—	—
2	50	96	91	0.36	23,000	14,000
3	100	48	70	0.29	—	—
4	100	96	89	0.38	—	—
5	100	120	94	0.54	30,000	17,000
6	150	96	85	0.47	—	—
7	150	192	90	0.63	39,000	24,000
8	200	96	82	0.51	—	—
9	200	192	93	0.55	—	—
10	300	96	76	0.62	38,000	24,000
11	300	192	88	0.67	—	—
12	300	96	66	0.72	50,000	36,000
13	300	192	81	0.85	65,000	50,000

*Initial monomer/initiator ratio.
†Measured with $c = 2$ g/l in dichloromethane at 25°C.
‡Determined by GPC (see Experimental part).
§Calculated from the Mark–Houwink equation of Ref. 4 on the basis of viscosity measurements in DMF at 30°C.

NMR spectroscopic measurements were conducted in a glove-box under an atmosphere of dry N_2.

Molecular weight measurements

The viscosities were measured in dichloromethane at 25°C by means of a thermostated Ubbelohde viscometer. The weight-average molecular weights were obtained from GPC measurements with four Ultrastyragel columns. A universal calibration curve was established by means of poly(styrene) standard (Macherey–Nagel Co.) measured in dichloromethane at 25°C. The molecular weights of the lactones were calculated from the maxima of their elution curves taking into account the intrinsic viscosities (Staudinger indices) measured in dichloromethane.

RESULTS AND DISCUSSION

Preparative aspects

In addition to halogenotrimethylsilanes, two trimethylsilyl esters of strong acids are commercially available, viz. bis-TMS-sulphate and TMS-triflate. Therefore, a first series of polymerizations was performed to compare the reactivity of these potential initiators. The results obtained with ϵ-caprolactone in 1,2-dichloroethane are summarized in Table 1. Although the reaction temperature was varied between 20 and 80°C, no polymerization was detectable with bis-TMS-sulphate as initiator. Higher temperatures are not advisable, because they favour the degradation of polylactones by back-biting [1, 4]. ^{1}H-NMR spectroscopic studies of bis-TMS-sulphate/ϵ-caprolactone or bis-TMS-sulphate/γ-butyrolactone mixtures (molar ratio 1:1) in deuterated chloroform confirmed that bis-TMS-sulphate is not reactive enough to attack five- or higher-membered lactones.

In a second series of experiments, ϵ-caprolactone was polymerized with TMS-triflate in 1,2-dichloroethane at 50°C (Table 2). This reaction temperature was chosen because the data of Table 1 and previous results obtained with methyltriflate [1] indicate that the rate of propagation is too low for preparative purposes at 20°C, whereas temperatures above 50°C favour degradation by back-biting [1, 4]. Variation of monomer/initiator ratio (M/I) and reaction time provided the following results. The polymerization is relatively slow, slower than the methyltriflate-initiated polymerization under identical conditions (Table 3). Three observations confirm that the lower yields obtained at short reaction times result from incomplete conversion. First, when compared at constant reaction time (96 hr), the yields decrease with increasing M/I ratio, because decreasing concentration of initiator at constant initial monomer concentration reduces the rates of initiation and propagation. Second, the yields increase with time at constant M/I ratio. Third, the molecular weights (inherent viscosities) increase with higher M/I ratios at constant time and with higher yields at constant M/I ratio.

The weight-average molecular weights ($\bar{M}_w$) of several poly(ϵ-caprolactone) samples were determined by means of GPC measurements. The GPC curves of all poly(ϵ-caprolactone) samples were monomodal, relatively narrow and nearly symmetrical. Commercially available poly(styrene) samples with $\bar{M}_w/\bar{M}_n$ ratios $\leqslant 1:1$ were used as standards, and a universal calibration curve was established by means of "Staudinger indices" measured in dichloromethane at 25°C. In this way $\bar{M}_w$s up to 65,000 were obtained (Table 2). For comparison, Staudinger indices of several poly(ϵ-caprolactone) samples were also measured in dimethylformamide (DMF) at 30°C, and $\bar{M}_w$s were calculated from the Mark–Houwink equation (6) [7]. This equation was established by Koleske *et al.* [7] on the basis of light-scattering and viscosity measurements in DMF. The $\bar{M}_w$ values calculated using Eqn (6) are significantly lower than those obtained by GPC in particular at the low end of the $\bar{M}_w$ range. Whatever is the reason for this discrepancy, it may be stated that cationic polymerization of ϵ-caprolactone may at least yield $\bar{M}_w$s around 50,000,

$$[\eta] = 1.91 \cdot 10^{-4} \times \bar{M}_w^{0.73} \quad (6)$$

Since the active chain ends of TMS-triflate and methyl-triflate initiated polylactones chains must be identical, yields and molecular weights should be similar provided that nearly identical reaction conditions and long reaction times enable comparable conversions. In order to test this hypothesis, methyltriflate initiated polymerizations of ϵ-caprolactone were conducted under conditions identical with those of Table 2. The results (Table 3) suggest for methyltriflate a higher rate of initiation, indicated by higher yields under conditions where TMS-triflate-initiated polymerizations are incomplete. Nevertheless, the viscosity and molecular weight measurements show satisfactory agreement.

TMS-triflate-initiated polymerizations of δ-valerolactone were conducted at 20°C, because a previous study of methyltriflate-initiated polymerizations had demonstrated that formation of cyclic oligomers by back-biting of the active chain end starts even at 50°C [4]. The results obtained at 20°C (Table 4) indicate that the polymerization of δ-valerolactone is slow and the conversion is far from 100% in all cases. The yields decrease continuously with increasing M/I-ratio. Compared with methyltriflate-initiated polymerizations conducted under identical conditions [4], TMS-triflate proves again to be the less effective initiator. In spite of low yields, the molecular weights ($\bar{M}_w$) reach values above 50,000 in agreement with values found for methyltriflate-initiated polymerizations [4].

In order to elucidate the role of the solvent, a few polymerizations were conducted in nitrobenzene (Table 5). For both monomers, higher yields were found at the highest M/I ratio, presumably because nitrobenzene slightly enhances the rate of poly-

Table 4. Polymerization of δ-valerolactone with TMS-triflate in 1,2-dichloroethane at 20°C (reaction hr)

No.	M/I*	Time (hr)	Yield (%)	η_{inh}† (dl/g)	η_{inh}‡ (dl/g)	$\bar{M}_n$§	$\bar{M}_w$¶
1	50:1	192	62	0.29	0.33	6651	—
2	100:1	192	55	0.32	0.37	8058	—
3	150:1	192	50	0.34	0.39	8870	—
4	200:1	192	41	0.41	0.48	13,660	39,000
5	300:1	192	38	0.44	0.54	18,214	—
6	400:1	192	36	0.54	0.62	26,735	58,000

*Initial monomer/initiator ratio.
†Measured with $c = 2$ g/l in dichloroethane at 25°C.
‡Measured with $c = 2$ g/l in chloroform at 20°C.
§Calculated from $\eta_{inh} = 0.48 \times \lg \bar{M}_n - 1.505$ according to Ref. 4.
¶Determined by means of GPC.

Table 5. TMS-triflate-initiated polymerizations of δ-valerolactone and ε-caprolactone in nitrobenzene

No.	Monomer	M/I	Temperature (°C)	Time (hr)	Yield (%)	η_{inh}* (dl/g)
1	δ-Valerol.	50:1	20	192	48	0.25
2	δ-Valerol.	100:1	20	192	56	0.30
3	δ-Valerol.	200:1	20	192	63	0.42
4	ε-Caprol.	50:1	50	192	90	0.52
5	ε-Caprol.	100:1	50	192	93	0.54
6	ε-Caprol.	200:1	50	192	96	0.58

*Measured with $c = 2$ g/l in dichloromethane at 25°C.

merization. However, the inherent viscosities are slightly lower than those obtained in 1,2-dichloroethane and thus nitrobenzene does not possess a particular advantage for preparative purposes, in as much as it is difficult to purify the poly(lactone)s from this high boiling solvent.

Mechanistic aspects

The preparative studies indicate that TMS-triflate is a less reactive initiator than methyltriflate. Since the active end groups of the growing chains must be identical, the different reactivities must concern the initiation step. In order to check this conclusion, 2:1 mixtures (molar ratios) of TMS-triflate and γ-butyrolactone, δ-valerolactone or ε-caprolactone were examined by i.r.- and ^{1}H-NMR spectroscopy.

$$CF_3—SO_2O—SiMe_3 + O{=}C\overset{(CH_2)_n}{\frown}O \rightarrow + Me_3Si—O—C^{\oplus}\overset{(CH_2)_n}{\frown}O + CF_3SO_3^{\ominus} \quad (7)$$

γ-Butyrolactone does not polymerize at room temperature for thermodynamic reasons, and thus its reaction with cationic initiator offers a good chance to study the initiation reaction without interference from subsequent propagation steps. i.r.-Spectra of a 2:1 mixture of TMS-triflate and γ-butyrolactone revealed a broadening of the carbonyl band, possibly indicating a weak interaction of the carbonyl oxygen with the silyl group. However, the band at 1610 cm^{-1} which represents dioxocarbenium ions formed according to Eqns (1) or (7) was never detectable (Fig. 1A and B). In contrast this band appeared within a few hours in the i.r.-spectra taken from 2:1 mixtures of methyltriflate and γ-butyrolactone (Fig. 1C).

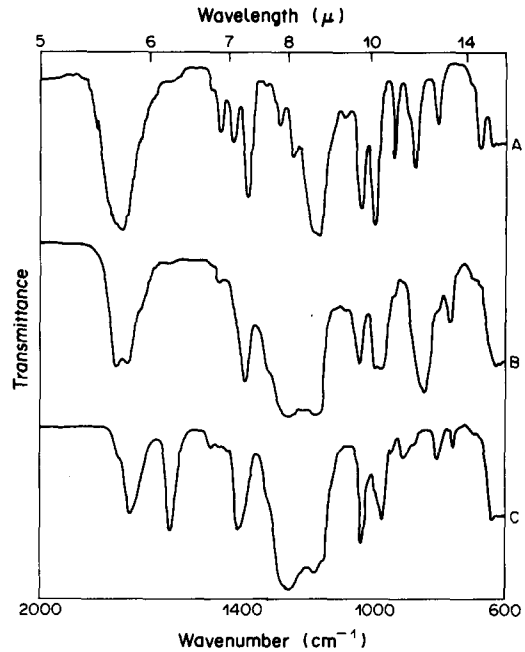


Fig. 1. i.r.-Spectra (measured between NaCl prisms): (A) pure γ-butyrolactone; (B) 2:1 mixture of TMS-triflate and γ-butyrolactone after 24 hr; (C) 2:1 mixture of methyltriflate and γ-butyrolactone after 24 hr.

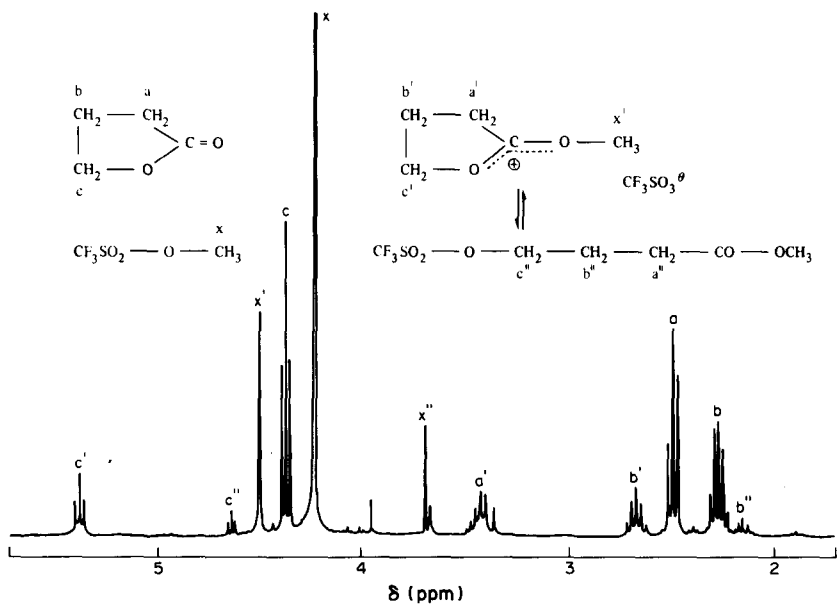


Fig. 2. 360 MHz ^{1}H-NMR spectrum (measured in $CDCl_2$) of a 2:1 mixture of methyltriflate and γ-butyrolactone after 24 hr.

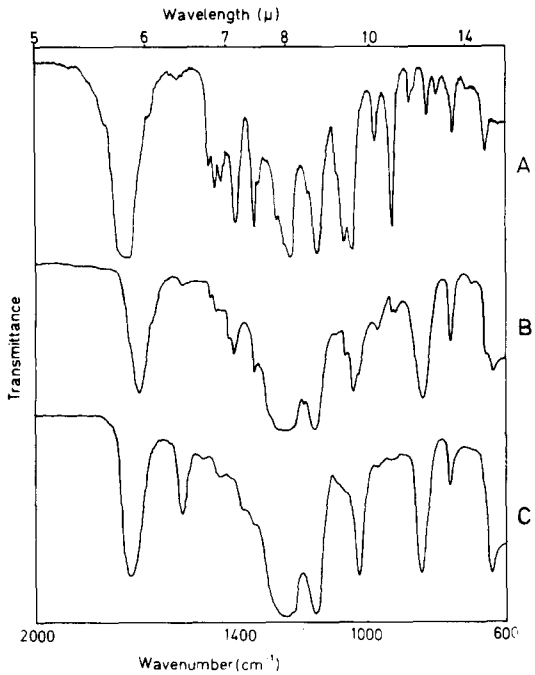


Fig. 3. i.r.-Spectra (measured between NaCl prisms): (A) pure δ-valerolactone; (B) 2:1 mixture of TMS-triflate and δ-valerolactone after 4 hr; (C) 2:1 mixture of TMS-triflate and δ-valerolactone after 24 hr.

^{1}H-NMR measurements of 2:1 mixtures in deuterated chloroform confirmed the i.r. results. No reaction was detectable in the case of TMS-triflate, whereas the characteristic signals of O-methylated γ-butyrolactone were observable in the case of methyltriflate (Fig. 2).

These results demonstrate that the initiation reaction of TMS-triflate, i.e. the silylation of lactones [Eqn (7)], is considerably less effective than the initiation of methyltriflate. Thus, the question arises

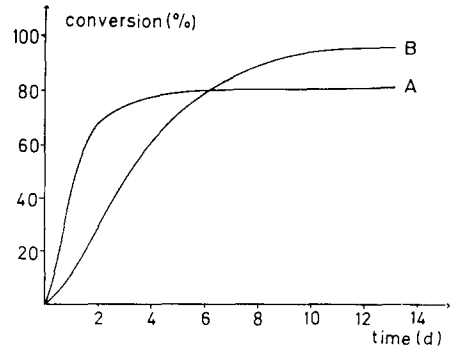


Fig. 5. Conversion/time curves of TMS-triflate initiated polymerizations of (A) δ-valerolactone and (B) ϵ-caprolactone in $CDCl_3$ at 20°C (M/I = 100; monomer concentration = 10 vol.%) determined by means of ^{1}H-NMR spectroscopy.

whether the low efficiency of the initiation step has kinetic or thermodynamic reasons. It is well known from organic silicon chemistry that nucleophilic substitutions of silyl groups possess significantly lower energies of activation than similar substitutions at alkyl groups, because the d-orbitals of the silicon favour nucleophilic attack. In consequence, nucleophilic substitutions of silyl groups are normally thermodynamically controlled reactions. In other words, the stability of silicon bonds governs the course of the reaction. The stability of bonds between a heteroatom and silicon depends in turn on the strength of the pπ-dπ-bond. From this point of view, it is evident that the positively charged oxygen of the dioxocarbeniumion in Eqn (7) is a less favourable substituent of the silicon than the triflate group. This means the silylation equilibrium of Eqn (7) is shifted to the left, whereas the analogous alkylation equilibrium of methyltriflate [Eqn (1)] is shifted to the right. Thus, the different efficiencies of TMS-triflate and methyltriflate as cationic initiators have a thermodynamic origin.

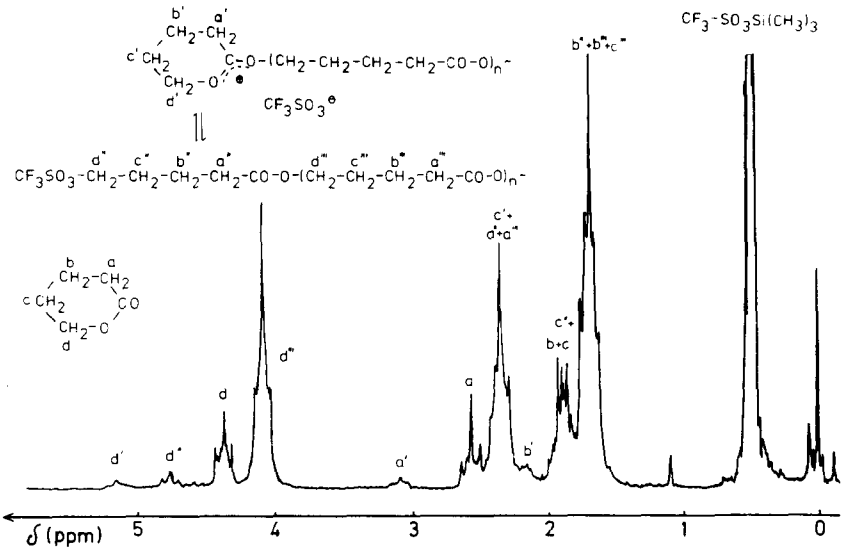


Fig. 4. 100 MHz ^{1}H-NMR spectrum (measured in $CDCl_2$) of a 2:1 mixture of TMS-triflate and δ-valerolactone after 24 hr.

i.r.-Spectra of TMS-triflate/δ-valerolactone mixtures agree with those of γ-butyrolactone in that a rapid initiation reaction is not detectable (Fig. 3A and B). Yet, when increasing viscosity of the reaction mixture indicates substantial polymerization (after 24 hr), the band at 1570 cm^{-1}, representing O-alkylated lactone, becomes detectable (Fig. 3C). The ^{1}H-NMR measurements agree with the i.r.-spectra. The typical signals of alkylated δ-valerolactone and its covalent isomer (Eqn 2) only become observable when a substantial fraction of the monomer was converted to polymer. Therefore, the signals of activate valerolactone units must originate from active chain ends and not from the initiation reaction (Fig. 4). The ^{1}H-NMR spectra also revealed that more than 95% of the TMS-triflate remains unchanged over the whole course of the polymerization. In other words, a slow initiation step is followed by a much faster propagation. This finding fits in with the observation that relatively high molecular weights are formed at low M/I ratios and low conversions (Table 4).

In the case of TMS-triflate/ϵ-caprolactone mixtures, neither i.r.-spectra nor 100 MHz ^{1}H-NMR spectra displayed bands or signals of activated species. However, the ^{1}H-NMR measurements of TMS-triflate-initiated polymerization of δ-valerolactone and ϵ-caprolactone conducted under identical conditions revealed that δ-valerolactone polymerizes more rapidly than ϵ-caprolactone (Fig. 5). This spectroscopic result perfectly agrees with previously published preparative results of methyltriflate initiated polymerizations [1, 2, 4]. Another satisfactory result of this comparison is the observation that the higher reactivity of δ-valerolactone in cationic polymerizations is paralleled by a higher sensitivity to degradation by back-biting.

CONCLUSIONS

The present study of TMS-triflate-initiated polymerizations of δ-valerolactone and ϵ-caprolactone leads to the following conclusions. TMS-triflate is a less effective initiator than methyltriflate (or triflic) acid because the first reaction step, i.e. the silylation of the lactone, is thermodynamically unfavourable. In consequence, propagation is significantly more rapid than initiation and, at low M/I-ratios, only a small fraction of TMS-triflate is consumed. Due to the slow initiation, TMS-triflate is for preparative purposes a less attractive initiator than methyltriflate (or triflic acid) although the molecular weights are as high or higher than those obtained with other initiators.

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