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POLYMERS OF CARBONIC ACID. 16. HIGH MOLECULAR WEIGHT POLY(NEOPENTANEDIOL CARBONATE) BY RING-OPENING POLYMERIZATION WITH *n*BuSnCl$_3$ OR SnOct$_2$ AS INITIATORS

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ABSTRACT

Neopentanediol carbonate, NPC, was polymerized in bulk at 120°C. Either *n*BuSnCl$_3$ or Sn(II)2-ethylhexanoate (SnOct$_2$) were used as initiators. The reaction time and the monomer/initiator (M/I) ratio were varied. Polymerizations initiated with *n*BuSnCl$_3$ were more rapid and yielded higher molecular weights (M_n up to 150,000 and M_w up to 270,000). Furthermore, the molecular weights were almost independent of the M/I ratio, provided the reaction time was optimized. In contrast, the molecular weights of the SnOct$_2$-initiated polymers paralled the M/I ratios more or less. This finding and the ^{1}H-NMR spectra suggest that stoichiometric reactions between monomer and SnOct$_2$ take place, yielding polymers with covalently bound octoate and OH endgroups. Finally, the polymerizability of NPC recrystallized from CCl$_4$ or from tetrahydrofuran was compared. No significant difference was found when *n*BuSnCl$_3$ was used as initiator, whereas in the case of SnOct$_2$ a difference was observed. NPC recrystallized from CCl$_4$ polymerized more rapidly and gave higher molecular weights than NPC recrystallized from THF.

INTRODUCTION

The present work is part of a broader study of Lewis acid-initiated polymerizations of lactones and cyclocarbonates. $SnOct_2$ is known to be a highly efficient initiator of L-lactide, and thus it has been the object of numerous investigations [1–10] and commercial applications [1–3]. However, preliminary studies of $SnOct_2$-initiated polymerizations of trimethylene carbonate have previously shown [11] that this initiator is less suited to produce high molecular weight polycarbonates. On the other hand, it has recently been found that nBuSnCl$_3$ is an excellent catalyst for the polymerization of trimethylene carbonate (TMC) [12]. Polymerizations of one monomer alone do not allow a final evaluation of catalysts. Therefore, it was the purpose of the present work to compare $SnOct_2$ and nBuSnCl$_3$ as initiators of NPC. Polymerizations of NPC have previously been studied by several research groups [13–20], but to the best of our knowledge nBuSnCl$_3$ and $SnOct_2$ have never been used as initiators.

EXPERIMENTAL

Materials

nBuSnCl$_3$ and $SnOct_2$ were purchased from Aldrich Co. (Milwaukee, WI, USA) and distilled in vacuo. NPC (5,5-dimethyl-1,3-dioxanone-2) was a gift of Bayer AG (Leverkusen, Germany). It was recrystallized either from CCl_4 (distilled over P_4O_{10}) or from tetrahydrofuran, THF (distilled over sodium), and ligroin. In both cases a melting point of 107–108°C was found. Gas chromatography revealed contaminations with residual CCl_4 around 2 mol% after drying at 65°C in vacuo. Only traces of THF (<0.1 mol%) were found.

Polymerizations

Freshly recrystallized NPC (50 mmol) was weighed into a 25-mL Erlenmeyer flask with silanized glass walls (pretreatment with Me_2SiCl_2). The initiator was added in the form of a 1 M solution in dry chloroform. The reaction vessel was completely immersed into an oil bath thermostated at 120°C. After cooling, the reaction product was dissolved in CH_2Cl_2 and precipitated into cold methanol. After filtration, the poly(neopentanediol carbonate) (polyNPC) was dried at 25°C in vacuo.

In a separate series of polymerizations the initiator was added in the form of a 1 M solution in toluene (see Table 3). The results of all these polymerizations are summarized in Tables 1–5.

Measurements

The inherent and intrinsic viscosities were measured with an automated Ubbelohde viscometer thermostated at 25°C. The DSC measurements were conducted with Perkin-Elmer DSC-7 in aluminum pans under nitrogen. The 360 MHz ^{1}H-NMR spectra were recorded with a Bruker AM-360 FT-NMR spectrometer in 5 mm o.d. sample tubes. The WAXD powder pattern was recorded with a Siemens D-500 diffractometer using Ni-filtered CuKα radiation.

The GC measurements were carried out on a Chrompack Md 438 S using a BPX5 column, a FID detector, and helium as the gas. The monomer was injected in the form of a highly concentrated solution in warm anisol. The extent of contamination with CCl_4 or tetrahydrofuran was estimated by comparison with NPC/anisol solutions purposely contaminated with 0.1, 0.5, 1.0, and 5.0 mol% of CCl_4 or tetrahydrofuran relative to NPC. GPC measurements were conducted in THF at 25°C. A combination of Ultrastyragel columns with pore sizes on the order of 50–1.500, 10^2–10^4, 2×10^2 to 30×10^3 and 5×10 to 600×10^3 Å were used along with differential refractometer Waters Md 410.

RESULTS AND DISCUSSION

Initiation with *n*BuSnCl$_3$

Preliminary experiments (not described here in detail) showed that *n*BuSnCl$_3$-initiated polymerizations of NPC in solution at moderate temperatures ($\leq$50°C) are too slow for preparative purposes. Therefore, all polymerizations for this work were conducted in bulk at higher temperatures quite analogous to our previous work with TMC [12]. A reaction temperature of 120°C was selected because the melting point of the monomer is 106–108°C and that of poly(NPC) in the 110 to 127°C range (depending on the molecular weight). Previous work with TMC has also revealed [21] that the polymerizability of this monomer depends on the purification procedure. TMC recrystallized from THF was purer and was thermally less stable than TMC recrystallized from CCl_4 or TMC distilled in vacuo. Therefore, two purification procedures were also used in this work, namely recrystallization from CCl_4 (yielding NPC-I) and recrystallization from THF (yielding NPC-II). Purification by recrystallization was preferred to sublimation (used by another research group [15–18]) for two reasons. First, sublimation is not an attractive purification procedure for larger quantities (>100 g) of monomers. Second, sublimation is not “a priori” a perfect purification. Its success depends on the properties of the potential contaminants, and only a careful comparison with other purification procedures can demonstrate if sublimation is the better alternative.

The GC analyses of the recrystallized NPC batches revealed a contamination of NPC with 1–2 mol% of CCl_4 after drying at 65°C in vacuo. A freshly recrystallized NPC quickly dried at 20°C may contain up to 5 mol% of CCl_4. Even higher values were found for TMC recrystallized from CCl_4, which cannot be dried above 40°C because of the low melting temperature. These observations suggest that CCl_4 has a particular affinity to aliphatic cyclo carbonates. In contrast, only traces of THF were found by GC in NPC, again in close analogy to TMC [21].

In a first series of *n*BuSnCl$_3$-initiated polymerizations, the M/I ratio was fixed at 200/1 and the reaction time was varied. The results, compiled in Table 1, are very similar for NPC-I and NPC-II. At the shortest reaction time (4 hours) the conversion is far from complete. The maximum yield (90–92%) was obtained after 8 hours and remained constant up to 48 hours. In contrast, the inherent viscosities decreased at long reaction times, suggesting that the chain growth process is followed by a slow backbiting degradation. The existence of transesterification processes is sup-

TABLE 1. *n*BuSnCl$_3$-Initiated Polymerizations of NPC in Bulk at 120°C (M/I = 200/1) with Variation of the Reaction Time

NPC recrystallized from CCl$_4$				NPC recrystallized from THF			
No.	Time, hours	Yield, %	η_{inh}, dL/g[a]	No.	Time, hours	Yield, %	η_{inh}, dL/g[a]
1	4	46-48[b]	0.60-0.68[b]	6	4	39-44[c]	0.80-0.85[c]
2	8	90-92[b]	0.99-1.04[b]	7	8	89-91[c]	1.00-1.10[c]
3	20	91-92[b]	1.00-1.12[b]	8	20	89-91[c]	1.35-1.45[c]
4	25	90	0.97	9	25	89	1.02
5	48	90-92[b]	0.66-0.71[b]	10	48	88-90[c]	0.88-0.92[c]

[a] Measured at 20°C with c = 2 g/L in CH$_2$Cl$_2$.

[b] Two polymerizations with different batches of NPC were conducted.

[c] Three polymerizations with different batches of monomers were conducted.

ported by GPC measurements indicating that the molecular weight distribution slightly broadened when the reaction time was increased from 8 to 48 hours. Furthermore, it is evident that the viscosities resulting from polymerizations of NPC-I were all slightly lower than those obtained from NPC-II at identical reaction times. Nonetheless, these results prove that contamination with CCl$_4$ does not hinder the formation of high molecular weights (see below). This finding is not suprising considering that CCl$_4$ is absolutely inert in the case of an insertion mechanism [12]. Even in the case of a cationic mechanism CCl$_4$ should be inert, because the trioxocarbenium ions formed as active chain ends are highly stabilized by delocalization.

A second series of polymerizations was designed to elucidate the influence of the M/I ratio. Again the experiments conducted with NPC-I (Table 2) and NPC-II

TABLE 2. *n*BuSnCl$_3$-Initiated Polymerizations of NPC (recrystallized from THF) in Bulk at 120°C with Variation of the M/I Ratio

Reaction time, 8 hours				Reaction time, 20 hours			
No.	M/I	Yield, %	η_{inh}, dL/g[a]	No.	M/I	Yield, %	η_{inh}, dL/g[a]
1	50	90	0.62	8	50	89	0.63
2	100	89	0.82	9	100	89	0.79
3	200	91	1.09	10	200	90	1.32
4	300	88	1.26	11	300	91	1.39
5	500	73	0.92	12	500	91	1.37
6	800	52	0.75	13	800	82	1.03
7	1200	0	—	14	1200	55	0.63

[a] Measured at 20°C with c = 2 g/L in CH$_2$Cl$_2$.

(Table 3) show the same trends. Both yields and viscosities decrease at M/I ratios above 300 when the reaction time is relatively short (8 hours). Longer reaction times (20 hours) gave higher yields and higher viscosities for M/I ratios >300. This means that high M/I ratios require reaction times of 20 hours for complete conversion. With a reaction time of 20 hours the yields proved to be almost constant for M/Is in the 50 to 500 range. The viscosities pass through a flat maximum at M/Is in the 200 to 800 range. Even if one takes into account that the conversions at M/I = 800 were not 100%, the data of Tables 2 and 3 clearly demonstrate that the molecular weights do not parallel the M/I ratios. This result agrees with those obtained from $SnCl_4$-, *n*$BuSnCl_3$-, and Bu_2SnCl_2-initiated polymerizations of TMC [21, 22].

In a third and fourth series of polymerizations the initiator *n*$BuSnCl_3$ was added to the neat monomer in the form of a 1 M solution in toluene (instead of chloroform). Surprisingly, the inherent viscosities of the isolated polyNPC samples were considerably lower regardless if NPC-I or NPC-II was used (Table 3). A speculative explanation can only be offered in connection with a cationic mechanism. Whereas $CHCl_3$ and CCl_4 are certainly inert against trioxocarbenium ions, toluene might react as a nucleophile and thus as a chain stopper.

$$[\eta] = 8.32 \times 10^{-3} \times M_w^{0.79} \text{ (in THF)} \tag{1}$$

$$[\eta] = 1.25 \times 10^{-4} \times M_w^{0.717} \text{ (in THF)} \tag{2}$$

$$[\eta] = 2.77 \times 10^{-4} \times M_w^{0.677} \text{ (in THF)} \tag{3}$$

In order to learn how high the molecular weights of *n*$BuSnCl_3$-initiated polyNPC may be, the Staudinger index of Sample 8, Table 1 ($[\eta] = 1.154$) was measured in THF. Based on this $[\eta]$ value, the viscosity-average molecular weight (M_v) was calculated via the Mark-Houwink equation (1). This equation is based on light-scattering measurements [15], and the M_v values thus obtained are close but slightly lower than the weight-average molecular weights (M_w). In this way a M_v of 520×10^3 was obtained. Furthermore, direct GPC measurements were conducted in THF at 25°C and calibrated with polystyrene standards. The *a* and *K* values of Eq. (2) reported for solutions of polystyrene in THF [23] were used for evaluation of the GPC curve. In this way a number-average molecular weight (M_n) of 150 ×

TABLE 3. *n*$BuSnCl_3$-Initiated Polymerizations of NPC in Bulk at 120°C. The Initiator Was Added in the Form of 1 M Solution in Toluene (M/I = 200/1)

NPC recrystallized from CCl_4				NPC recrystallized from THF			
No.	Time, hours	Yield, %	η_{inh}, dL/g[a]	No.	Time, hours	Yield, %	η_{inh}, dL/g[a]
1	4	48	0.58	5	4	43	0.64
2	8	86	0.67	6	8	86	0.83
3	20	88	0.69	7	20	87	0.81
4	48	85	0.60	8	48	89	0.75

[a] Measured at 20°C with *c* = 2 g/L in CH_2Cl_2.

10^3 and a M_w of 270 × 10^3 was found. Finally, the Mark-Houwink equation (3) reported for solutions of poly(trimethylene carbonate) in THF [24] was used for a calculation of M_v from $[\eta] = 1.154$. In this way a M_v of 220 × 10^3 was obtained, in good agreement with the M_w of 270 × 10^3. Regardless which value is closest to the truth, it is obvious that Sample 8, Table 1, has a $M_w > 220 \times 10^3$. The highest value reported for an anionic polymerization of NPC amounts to $M_w = 120 \times 10^3$ [15]. The molecular weights reported for cationic polymerizations of NPC so far are even much lower ($< 10 \times 10^3$). Thus the molecular weights obtained in this work are the highest reported in the open literature. This result is not surprising, because both anionic and cationic polymerizations of NPC are plagued by rapid backbiting degradation even at low temperatures. Also in the case of trimethylene carbonate, lactide and lactone catalysts initiating an insertion mechanism yield higher molecular weights than initiators of anionic or cationic polymerizations.

The high molecular weight determined for Sample 8, Table 1, fits in with a high melting temperature. As illustrated in Fig. 1, the DSC mesurements revealed two endotherms in the first heating trace resulting from the melting of crystallites of two different modifications. The existence of two crystal modifications in the case of polyNPC is well documented in the literature [14, 15, 26]. After cooling from the melt, only the thermodynamically more stable modification was obtained (as usual

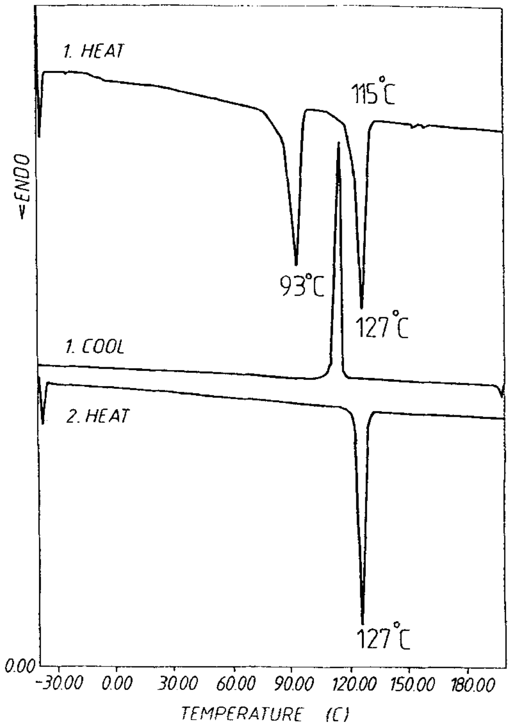


FIG. 1. DSC measurements (heating/cooling rate 20°C/min) of polyNPC 8, Table 1. First heating of the polymer dried at 65°C; second heating after cooling from the first heating.

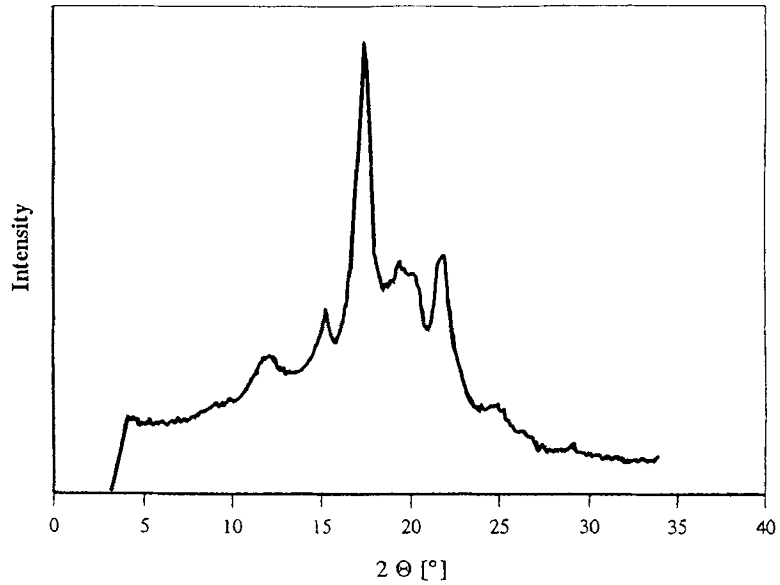


FIG. 2. WAXD powder pattern of polyNPC 8, Table 1.

[15, 25, 26] with a melting temperature (T_m) of 127°C). To the best of our knowledge, this is the highest T_m reported so far. The DSC measurements also seem to indicate a high degree of crystallinity. Therefore, WAXS powder patterns were measured after annealing at 65°C. However, these WAXS patterns (Fig. 2) only indicate a degree of crystallinity around 50%.

TABLE 4. $SnOct_2$-Initiated Polymerizations of NPC-I (recrystallized from CCl_4) in Bulk at 120°C with Variation of the M/I Ratio

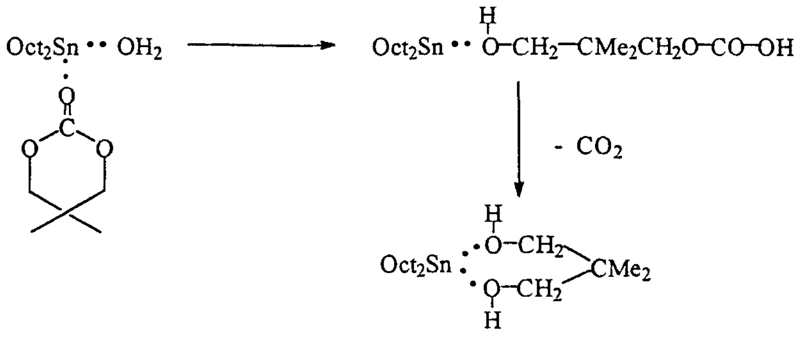
Reaction time, 8 hours				Reaction time, 20 hours			
No.	M/I	Yield, %	η_{inh}, dL/g[a]	No.	M/I	Yield, %	η_{inh}, dL/g[a]
1	50	90	0.79	8	50	91	0.81
2	100	91	1.02	9	100	90	1.04
3	200	90	1.07	10	200	88	1.15
4	300	84	1.16	11	300	90	1.22
5	500	77	0.64	12	500	88	1.28
6	800	62	0.58	13	800	75	1.16
7	1200	0	—	14	1200	51	0.52

[a] Measured at 20°C with $c = 2$ g/L in CH_2Cl_2.

Initiation with SnOct$_2$

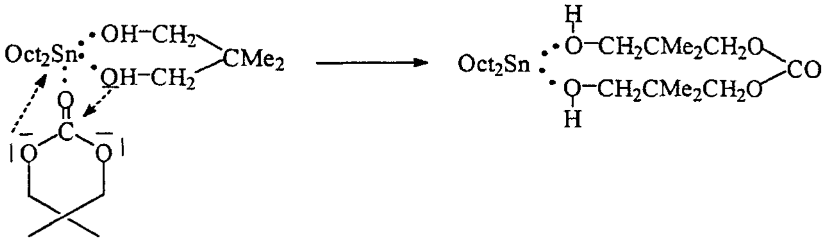
With SnOct$_2$ as initiator and NPC-II as monomer, several polymerizations were conducted in bulk at 120°C with reaction times of 4 and 8 hours. At M/I ratios of 200/1 or 500/1 no yields above 10% were obtained. These negative results and the results compiled in Tables 4 and 5 prove that SnOct$_2$ is less reactive as an initiator of NPC than is *n*BuSnCl$_3$. In the case of NPC-II and with M/I ratios $\geq$ 100, even a reaction time of 20 hours does not suffice for a complete conversion of the monomer.

Somewhat surprising are the differences found for polymerizations conducted with NPC-I (Table 4) and those conducted with NPC-II (Table 5). In the case of NPC-I, the M/I ratio has relatively little influence on the inherent viscosity up to a M/I of 500 regardless of the reaction time. This aspect and the rather high viscosities resemble the results found for *n*BuSnCl$_3$-initited polymerization of NPC-I and NPC-II (Tables 1 and 2). However, when NPC-II (recrystallized from THF) was polymerized with SnOct$_2$, the viscosities displayed a considerable dependence on the M/I ratio (Table 5) and all polymerizations were slower. The latter result may be explained by the assumption that the small amounts of THF (approx. 0.1 mol%) which remains in the recrystallized NPC react as ligands with SnOct$_2$ which is a strong Lewis acid. However, this process does not explain the strong influence of the M/I ratio on the molecular weights. Obviously, a stoichiometric reaction between SnOct$_2$ and the monomer takes place which limits the molecular weights. Two stoichiometric reactions can take place: (A) the reaction with water which remains bound to SnOct$_2$ even after storage over P_4O_{10} [10] (Eqs. 4–6).



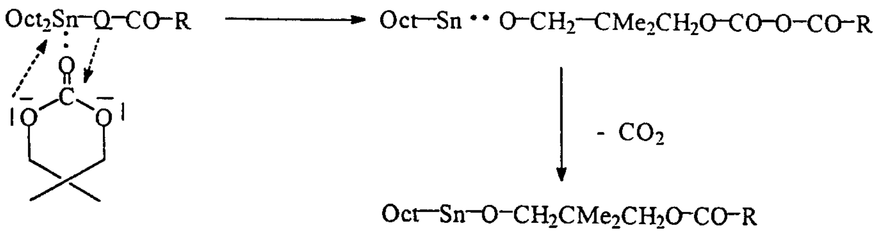
(4)

(5)



(6)

(B) The reaction with an octoate group (Eqs. 7–9).



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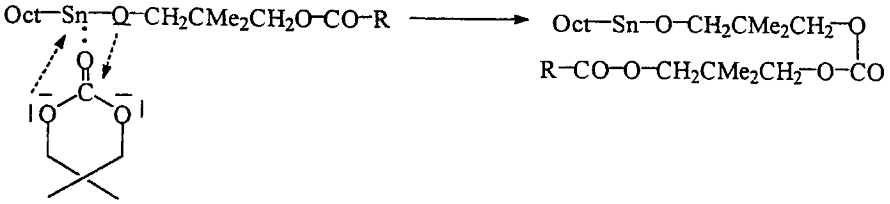

(9)

High resolution ^{1}H-NMR spectra of polyNPC samples isolated from the experiments of Table 5 indeed exhibit the signals of CH_2—OH endgroups and of octoate endgroups (Fig. 3). Both kinds of endgroups have also been found in $SnOct_2$-initiated poly(trimethylene carbonate) [11]. Therefore, it is obvious that stoichiometric reactions such as those outlined in Eqs. (2)-(7) may occur, but it is difficult to understand why they play a minor role in the polymerizations of NPC-I. However, a more detailed study of the polymerization mechanisms and the potential side reactions of $SnOct_2$ was not intended in this work, because the results found here and in previous work [12] demonstrate that *n*$BuSnCl_3$ is the more attractive initiator.

TABLE 5. $SnOct_2$-Initiated Polymerizations of NPC-II (recrystallized from THF) in Bulk at 120°C with Variation of the M/I Ratio

Reaction time, 20 hours				Reaction time, 70 hours			
No.	M/I	Yield, %	η_{inh}, dL/g[a]	No.	M/I	Yield, %	η_{inh}, dL/g[a]
1	50	93	0.19	8	50	94	0.18
2	100	92	0.37	9	100	93	0.37
3	200	86	0.49	10	200	90	0.52
4	300	82	0.58	11	300	91	0.66
5	500	65	0.60	12	500	92	1.06
6	800	50	0.45	13	800	80	0.92
7	1200	0	—	14	1200	61	0.64

[a] Measured at 20°C with $c = 2$ g/L in CH_2Cl_2.

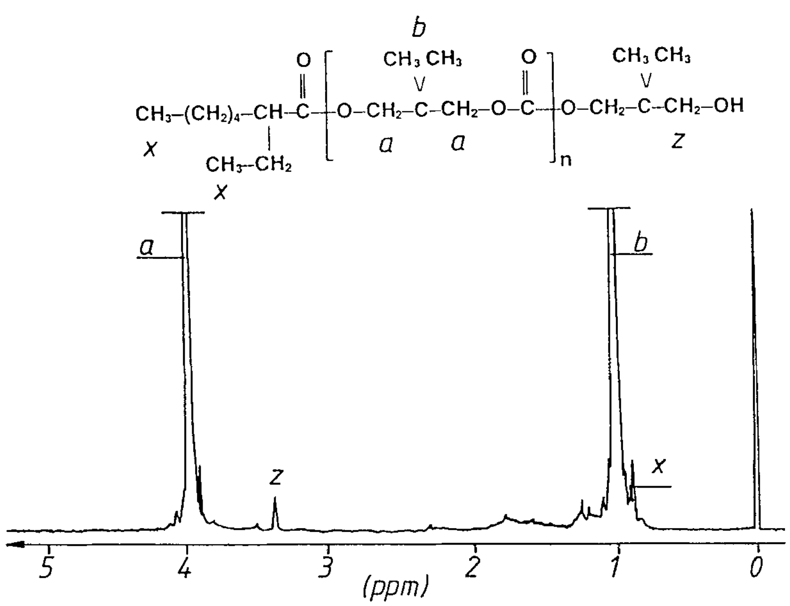

FIG. 3. 360 MHz ^{1}H-NMR spectrum of polyNPC 2, Table 4.

CONCLUSION

The present study demonstrates that both tin compounds *n*BuSnCl$_3$ and SnOct$_2$ are useful initiators for the polymerization of NPC. The yields and molecular weights obtained with SnOct$_2$ are higher than expected on the basis of a previous study [11] using trimethylene carbonate as monomer. However, *n*BuSnCl$_3$ proved to be the more useful initiator because it produces higher molecular weights and its reactivity is more reproducible. In the case of SnOct$_2$ the reactivity depends on pretreatment, such as distillation or the duration and conditions of storage.

REFERENCES

[1] E. E. Schmitt and R. A. Polistina, US Patent 3,297,033 (1967) to American Cyanamid Co.; *Chem. Abstr., 66*, P38656u (1967).
[2] E. E. Schmitt and R. A. Polistina, US Patent 3,463,158 (1969) to American Cyanamid Co.; *Chem. Abstr., 71*, P92382t (1969).
[3] Ethicon Inc., German Offen. 2,162,900 (1972); *Chem. Abstr., 76*, P73051w (1972).
[4] B. Ething, S. Gobolewski, and A. J. Pennings, *Polymer, 23*, 1587 (1982).
[5] F. E. Kahn, J. G. van Ommen, and J. Feijen, *Eur. Polym. J., 19*, 1081 (1983).
[6] R. Vasantharamari and A. J. Pennings, *Polymer, 24*, 175 (1983).
[7] A. J. Nijenhuis, D. W. Grijpma, and A. J. Pennings, *Macromolecules, 25*, 2419 (1992).
[8] G. Rafler and J. Dahlmann, *Acta Polym., 41*, 611 (1990).

[9] J. Dahlmann and G. Rafler, *Ibid., 44,* 103 (1993).

[10] H. R. Kricheldorf, I. Kreiser-Saunders, and C. Boettcher, *Polymer, 36,* 1253 (1995).

[11] H. R. Kricheldorf, J. Jenssen, and I. Kreiser-Saunders, *Makromol. Chem., 192,* 2391 (1991).

[12] H. R. Kricheldorf and B. Weegen-Schulz, *J. Polym. Sci., Part A, Polym. Chem., 33,* 2193 (1995).

[13] S. J. Rajan, US Patent 4,423,205 (1983) to Ethyl Corp.; *Chem. Abstr., 100,* 121805h (1984).

[14] H. R. Kricheldorf, R. Dunsing, and A. Serra i Albet, *Makromol. Chem., 188,* 2453 (1987).

[15] H. Keul, R. Bäcker, and H. Höcker, *Ibid., 187,* 2579 (1986).

[16] W. Hovestadat, A. J. Müller, H. Keul, and H. Höcker, *Makromol. Chem., Rapid Commun., 11,* 271 (1990).

[17] A. J. Müller, H. Keul, and H. Höcker, *Eur. Polym. J., 27,* 1323 (1991).

[18] W. Hovestadt, H. Keul, and H. Höcker, *Polymer, 33,* 1941 (1992).

[19] K. E. Piejko, B. Boemer, H. J. Buysch, and M. Huellmann, European Patent Appl. 299,305 (1989) to Bayer AG; *Chem. Abstr., 111,* 58527d (1989).

[20] N. J. Boyle Jr., F. Mares, J. M. Patel, and R. T. H. Tang, WO 8905.664 (1989) to Allied Signal Inc.; *Chem. Abstr., 111,* 240554h (1989).

[21] H. R. Kricheldorf, B. Weegen-Schulz, and S.-R. Lee, "Polymers of Carbonic Acid. 12," *Makromol. Chem.*, In Press.

[22] H. R. Kricheldorf and B. Weegen-Schulz, "Polymers of Carbonic Acid. 13," *Polymer*, In Press.

[23] J. A. P. P. van Dijk, J. A. M. Smit, F. E. Kohn, and J. Feijen, *J. Polym. Sci., Polym. Chem. Ed., 21,* 197 (1983).

[24] K. J. Zhu, R. W. Hendren, K. Jensen, and G. C. Pitt, *Macromolecules, 24,* 1736 (1991).

[25] H. R. Kricheldorf and J. Jenssen, *J. Macromol. Sci.—Chem., A26,* 631 (1989).

[26] S. Sarel and L. A. Pohoryles, *J. Am. Chem. Soc., 80,* 4596 (1958).

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