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A STUDY OF THE MECHANISMS AND KINETICS OF THE MOLTEN STATE REACTION OF NON-CATALYZED CYANATE AND EPOXY–CYANATE SYSTEMS

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Abstract—Molten state epoxy–cyanate reactions using non-catalyzed monofunctional models were analyzed in the temperature range of 150–250°C. In comparison to results obtained with paracumyl phenyl cyanate (CPCy), the present findings enabled the detection of four-membered ring and carbamate intermediates that autocatalyzed the reaction. Conclusions could be drawn only after preparative HPLC separation of the different fractions and analysis by ^{13}C-NMR, ^{1}H-NMR and FTIR. A new reaction path is proposed for these systems.

INTRODUCTION

Epoxy–cyanate reactions were examined in the temperature range of 150–250°C. Results published in 1964 [1] showed that copolymerization occurred in these conditions, with the formation of oxazole structures.

In 1987, Gotro *et al.* [2] having conducted an infrared spectroscopy study, reported the formation of cyclic iso-oxazole and postulated that homopolymerization reactions occurred in parallel. In 1988, Shimp *et al.* [3] showed that triazine, or aryl cyanurate (product from the trimerization of cyanates), was the reaction intermediate that further reacted on epoxy functions. Bauer *et al.* [4–6] proposed a complex mechanism based on the study of 4-chlorophenol cyanate and phenyl glycidyl ether model compounds. Shimp and Wentworth [7] recently reported results obtained with a model closer to dicyanate esters (i.e. p-cumyl phenyl cyanate) using GPC and FTIR in the presence of a catalyst. In the work reported below the authors have utilized published reaction paths for the attribution of the different peaks present in the GPC chromatograms.

In light of the number of proposed mechanisms and their low degree of concordance, we undertook a study of epoxy–cyanate systems using the monofunctional model compounds shown in Fig. 1. Since aryl cyanurate is a reaction intermediate, we simultaneously studied the homopolymerization reaction mechanisms of paracumyl phenyl cyanate (CPCy) in the molten state in the same temperature range.

EXPERIMENTAL

Raw materials

Paracumyl phenyl cyanate (CPCy) (ex Rhône Poulenc) and phenyl glycidyl ether (PGE) (ex Fluka) were purified by distillation.

Experimental techniques

(a) Kinetic experiments They were done in glass tubes containing a given quantity of the sample to be studied (≈200 mg) at 230°C for 24 hr. They were sealed under a nitrogen stream to avoid oxidations and/or side reactions occurring in the presence of humidity.

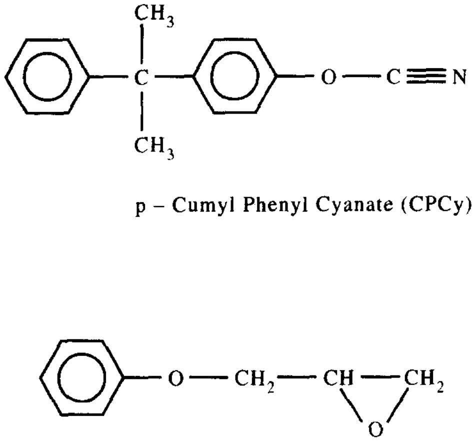
(b) Fourier transform infrared spectroscopy (FTIR). FTIR spectra were recorded using a Bruker IFS 45 spectrometer under the following conditions: spectral width 4000–400 $\mathrm{cm^{-1}}$, 32 accumulations, resolution 2 $\mathrm{cm^{-1}}$, triangular apodization signal processing. Depending on their physical state, samples were analyzed in the form of a film between two NaCl faces or mixed into a potassium bromide disk.

(c) Nuclear magnetic resonance (NMR). High resolution ^{1}H- and ^{13}C-NMR in liquids were recorded using a Bruker AM 400 spectrometer in the following conditions: 90° pulse angle (7 μsec for ^{1}H, 4.2 μsec for ^{13}C), digital resolution 0.122 Hz/point (^{1}H) and 0.375 Hz/point (^{13}C) equivalent to a spectral width of 4000 Hz (^{1}H) and 20,000 Hz (^{13}C) for a memory space of 64 kb (^{1}H) and 128 kb (^{13}C). Chemical shifts were given on the basis of tetramethylsilane (TMS) as internal standard. In order to attribute carbon classes (CH, CH_2, CH_3, quaternary) Distortionless Enhanced Polarization Transfer (DEPT) selective pulse sequences were used.

(d) High performance liquid chromatography (HPLC). The analyses were carried out using a Varian 5000 equipped with a variable wavelength detector set at the appropriate wavelength, or with a Varian 9010 coupled to a u.v. photodiode matrix detector. Quantitative determinations were made possible by the inclusion of an internal standard (chlorobenzene).

Conditions
Column: ODS-2, C_{18} bonded silica.
Eluent: water/methanol.
Programming: 70–100% of methanol in 20 min.
Detection wavelength: 254 nm.

(e) Differential scanning calorimetry (DSC). DSC thermograms were obtained with a Setaram DSC 111G programmable differential calorimeter set at a heating rate of 5°C/min.



p - Cumyl Phenyl Cyanate (CPCy)

Phenyl Glycidyl Ether (PGE)

Fig. 1. Model compounds studied.

RESULTS AND DISCUSSION

Study of CPCy homopolymerization in the molten state

Vibrational spectroscopy methods and NMR were used to follow reaction kinetics and mechanisms. According to the literature [7–9], the homopolymerization mechanism involves autocatalysis brought about by a mobile hydrogen group.

The HPLC study enabled the number of products in the reaction mixture to be evaluated. It can be seen that as the reaction advanced, CPCy disappeared and the aryl cyanurate peak increased (Fig. 2). After 30 min at 230°C, additional peaks were noted, corresponding to by-products or reaction intermediates. After 8 hr, it could be considered as a first approximation that there were three compounds in the medium, one of which was the majority (aryl cyanurate at 60%), whereas initial monomer was no longer detectable at 4 hr. The entities created were quantified (Fig. 3) in comparison to the internal standard.

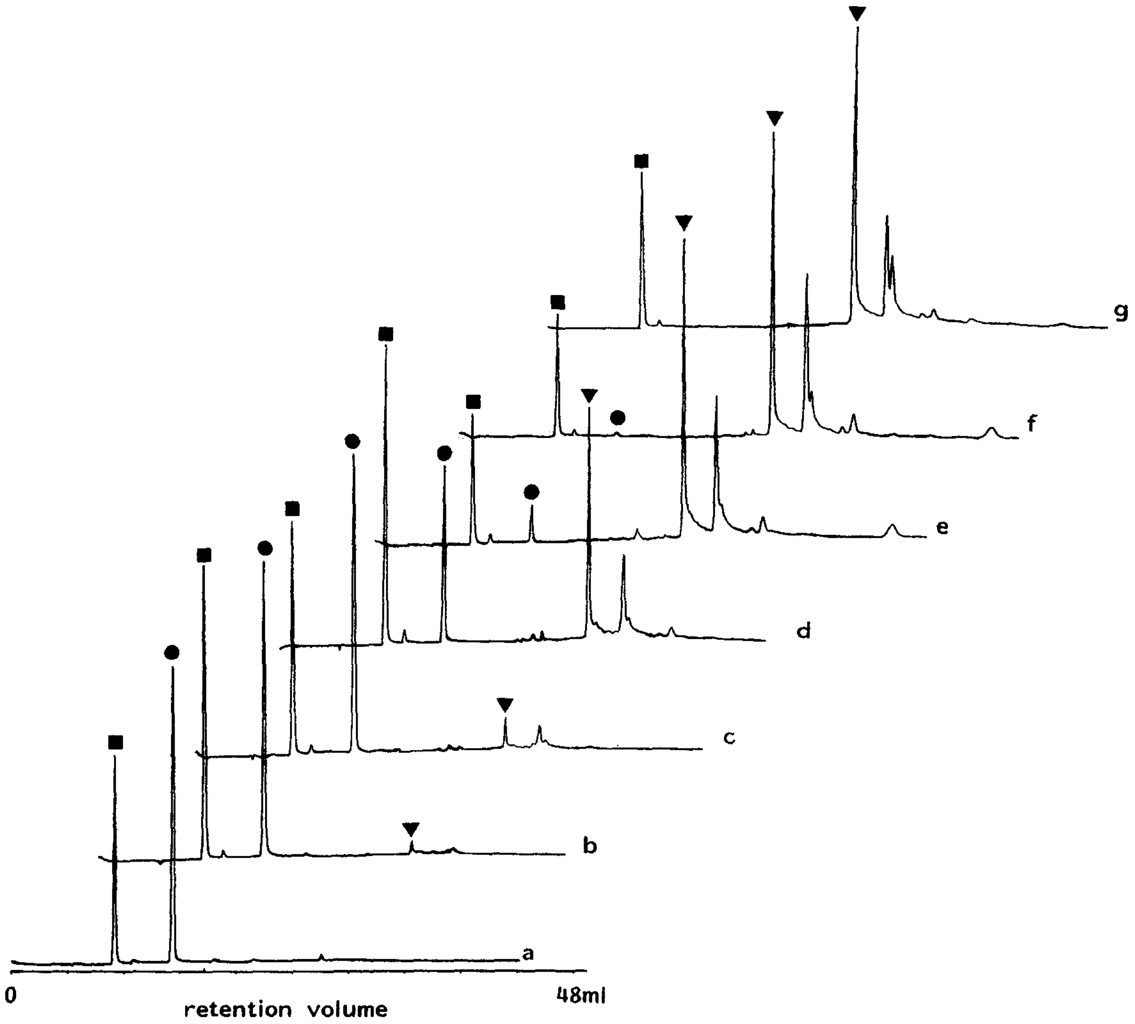


Fig. 2. Kinetics of CPCy at 230°C followed by HPLC.(■) Chlorobenzene (standard); (●) CPCy; and (▼) aryl cyanurate. a: $t = 0$; b: $t = 0$ hr 15; c: $t = 0$ hr 30; d: $t = 1$ hr 00; e: $t = 2$ hr 00; f: $t = 4$ hr 00; and g: $t = 8$ hr 00.

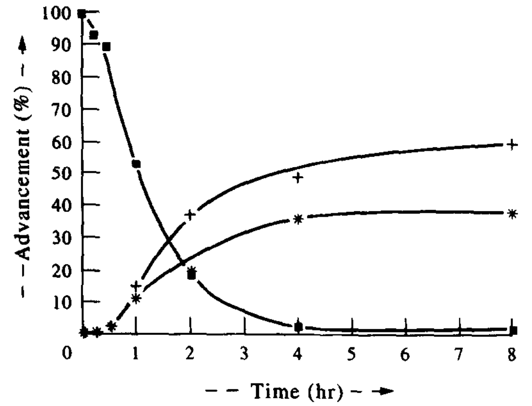


Fig. 3. Kinetic curves of CPCy at 230°C obtained by HPLC. (■) CPCy; (+) aryl cyanurate; (*) by-products.

Table 1 lists the ^{13}C-NMR chemical shifts obtained in the spectrum of the monomer at time zero and during kinetics, those of synthetic and purified aryl cyanurate, as well as those of the intermediates carbamate and monophenol that may participate in the reaction mixture.

In ^{13}C-NMR, the characteristic line of the cyanate function was located at 108.8 ppm. In the course of the reaction, all the CPCy lines diminished and disappeared (except carbon 11), and new lines appeared. By comparison with the chemical shifts of aryl cyanurate (Fig. 4), it was possible to detect two other secondary products, but which could be reaction intermediates. This is seen above all in the 175–160 ppm region, where three lines were found instead of the single line expected. This is more pronounced in the 45–30 ppm region, where isopropyl group carbons resonate, leading to the perfect quantization of monomer disappearance and the appearance of aryl cyanurate and secondary products, as described in the literature [10].

Changes in quaternary C_6 (42.7 ppm) and methyl group carbons C_7 (30.7 ppm) were followed with time. During evolution of the reaction medium, these two resonance lines decreased and disappeared, while for each carbon three other lines appeared, one of which was attributed to the isopropyl group of the aryl cyanurate ring.

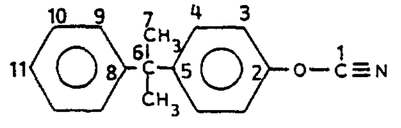
The chemical shifts in the proton spectrum (Table 2) of pure aryl cyanurate in comparison to that of

Table 1. ^{13}C-NMR chemical shifts of CPCy, cumyl phenol, cumyl carbamate and aryl cyanurate

compounds	**chemical shifts (δ PPM)**										
(a)	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
1	108.9_3	150.7_7	114.3_8	128.7_5	149.6_2	42.7_6	30.4_2	149.8_2	126.6_2	128.8_3	126.7_0
2	-	153.1_4	115.4_3	126.8_8	143.4_8	42.5_4	31.1_4	151.1_4	126.8_8	128.3_1	125.8_4
3	155.5_7	150.7_3	121.1_5	127.7_1	147.9_1	42.5_8	30.7_4	148.4_5	125.6_4	127.9_7	126.6_9
4	173.5_1	149.5_5	121.0_1	126.9_0	148.4_6	42.7_6	30.8_5	150.2_3	125.9_1	128.2_0	126.7_0

(a) molecules

1



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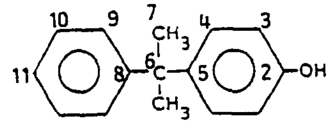

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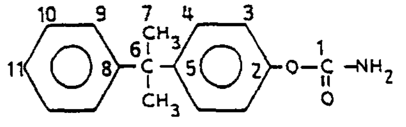

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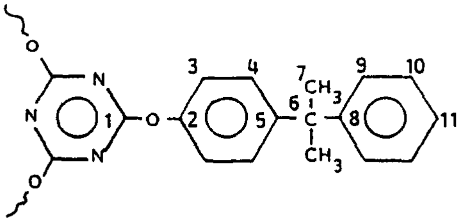


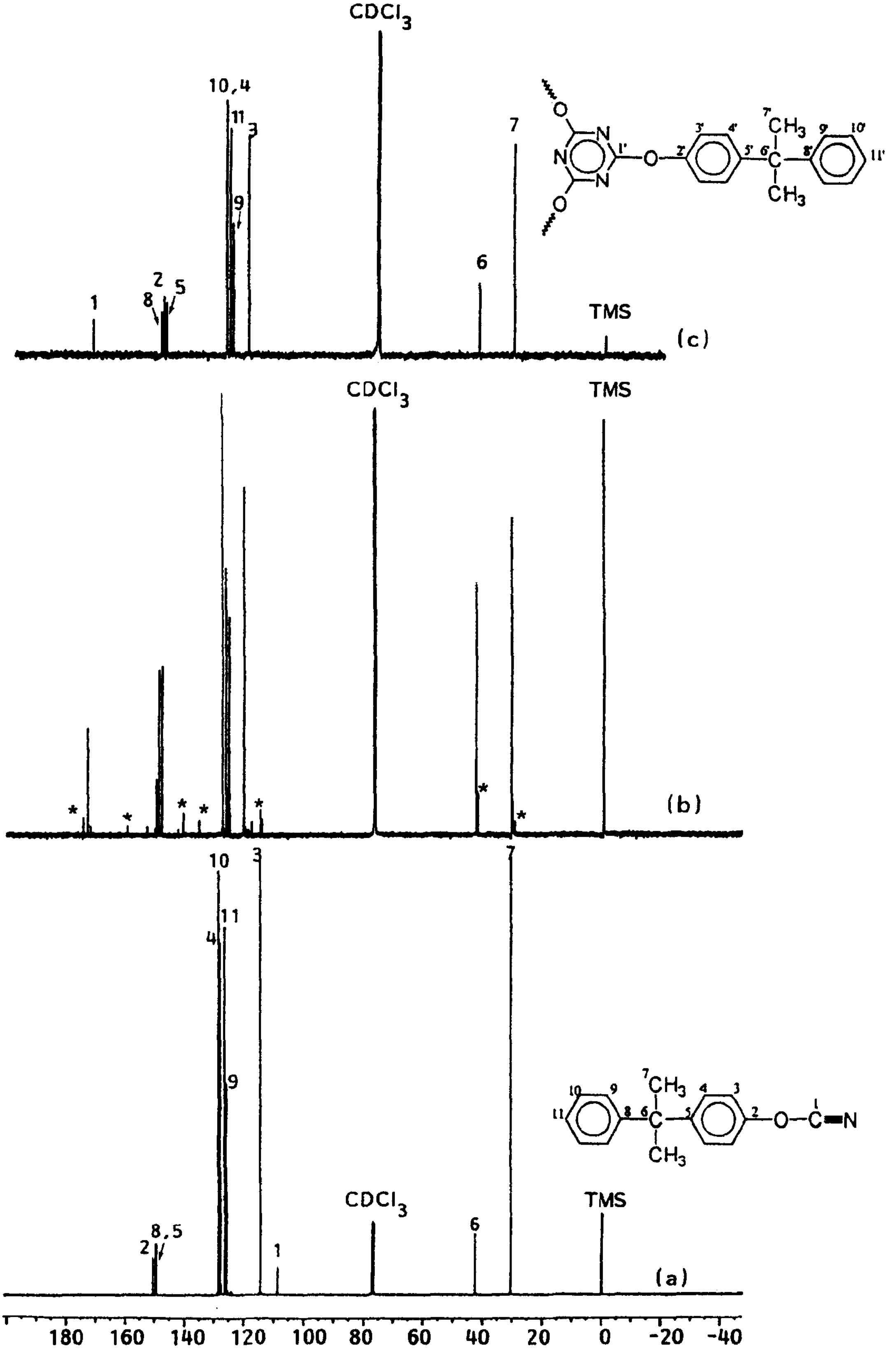


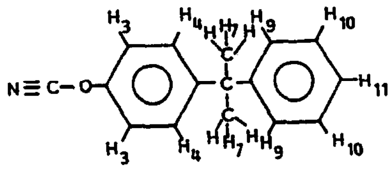
Fig. 4. ^{13}C-NMR spectra (CPCy, CPCy 24 hr at 230°C, purified aryl cyanurate). a: CPCy; b: CPCy 24 hr at 230°C (* reaction intermediates); and c: purified aryl cyanurate.

Table 2. ^{1}H-NMR chemical shifts of CPCy, cumyl phenol, cumyl carbamate and aryl cyanurate

compounds	**chemical shifts (δ PPM)**						
(b)	H_1	H_3	H_4	H_7	H_9	H_{10}	H_{11}
1	-	7.1_8	7.1_9	1.6_7	7.2_8	7.2_7	7.1_7
2	6.0_4	6.6_7	7.0_3	1.5_9	7.1_9	7.2_0	7.1_1
3	-	7.0_1	7.2_1	1.6_6	7.2_3	7.2_4	7.1_6
4	-	7.0_4	7.1_9	1.6_6	7.2_3	7.2_4	7.1_8

(b) molecules

1



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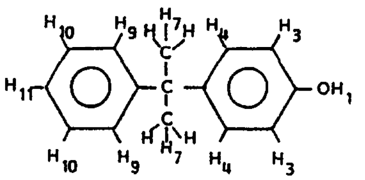

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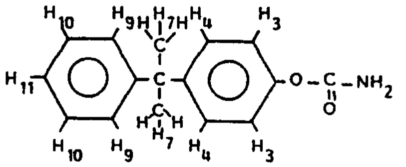

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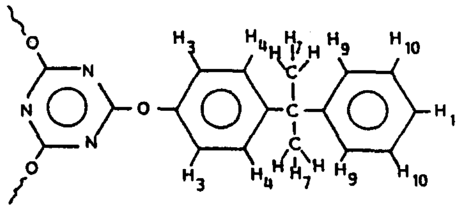


CPCy in the region of aromatic protons (8–6.8 ppm) showed that protons H_3 to the aryl cyanurate ring resonated at higher field than those of the initial CPCy. Quantifying these signals during the heat cycle showed that after 5 hr at 230°C, triazine ring formation advanced 65%. The presence of two doublets around 6.7 ppm was noted, however, attributed to reaction intermediates since they were absent in the initial CPCy spectra and in that of purified aryl cyanurate. These intermediates were identified in the study of epoxy–cyanate reactions, the first attributed to a four-membered ring, the second to protons H_3 of phenol present in the initial CPCy. The same method was used in the region of aliphatic protons, 1.5–1.7 ppm, where the two methyls of the isopropyl group resonated as a singlet. The formation of the different products with time was shown by the appearance of several singlets in this region, the signal from the aryl cyanurate molecule being the strongest (Fig. 5). Quantifying all the ^{13}C- and ^{1}H-NMR signals enabled changes in the reaction medium to be followed at the level of the disappearance of CPCy, at that of the appearance of aryl cyanurate and the secondary products (Fig. 6).

It is noted that the quantization of secondary products with time is a curve with a maximum, suggesting that they are reaction intermediates regardless of the ring examined.

Based on the FTIR spectrum of pure aryl cyanurate and of CPCy, we are able to select lines suitable for a kinetic study. Each new or residual species was quantified by using as a reference band that of the out-of-plane deformation of CH groups in the monosubstituted aromatic ring at 700 cm^{-1}, since it remained well defined with no shoulder throughout the kinetics and independent of participating mechanisms. The disappearance of CPCy was characterized by changes in the double line at 2270 and 2234 cm^{-1}.

During the homopolymerization reaction, the C≡N triple bond opened and aryl cyanurate formed, whose characteristic bands were situated towards 1569 cm^{-1} (νC═N—C) and 1385 cm^{-1} (νN—C—O).

FTIR spectra were similar to those observed with HPLC and ^{1}H- and ^{13}C-NMR, confirming the presence of reaction intermediates that were not iminocarbonates (Fig. 6).

In order to confirm this result, DSC was carried out on a sample recovered after 24 hr at 230°C, containing 60% aryl cyanurate and 40% by-products. When the thermograms obtained with CPCy alone were compared to those of the partially polymerized product in the same temperature range and the same experimental conditions [Fig. 7(a)], this product exhibited an exotherm for intermediates starting around 90°C and an endotherm around 150°C (melting of the aryl cyanurate).

This very important result for the homopolymerization study of CPCy indicates that:

(a) aryl cyanurate rings auto-accelerate reaction kinetics

(b) the other products present in the reaction mixture are reaction intermediates that rearrange to aryl cyanurate at the end of the heat cycle.

The homopolymerization kinetics of CPCy were followed isothermally at 200, 205, 210 and 220°C (Fig. 8). Kinetic curves could be simulated with an equation of the form:

$$v = dx/dt = k(1-x)^2 + k_1 x(1-x)^2 \text{ (mol/hr)}$$

initiation autocatalysis

Although the term k_1 was obtained with good correlation coefficients, there was considerable inaccuracy in the term k. By processing ln k vs $1/T$ curves, activation energies of the order of 85.9 kJ/mol were found for k_1, in agreement with published data [10].

Study of the copolymerization of the epoxy–cyanate (1/1) in the molten state

The DSC thermograms obtained for the homopolymerization of CPCy and CPCy/PGE (1/1) [Fig. 7(b)] show that the presence of epoxy groups catalyzed the system, since the starting temperature of the reaction was lowered by about 30°C in comparison to that of CPCy homopolymerization. In addition, the CPCy/PGE thermogram shows a double envelope,

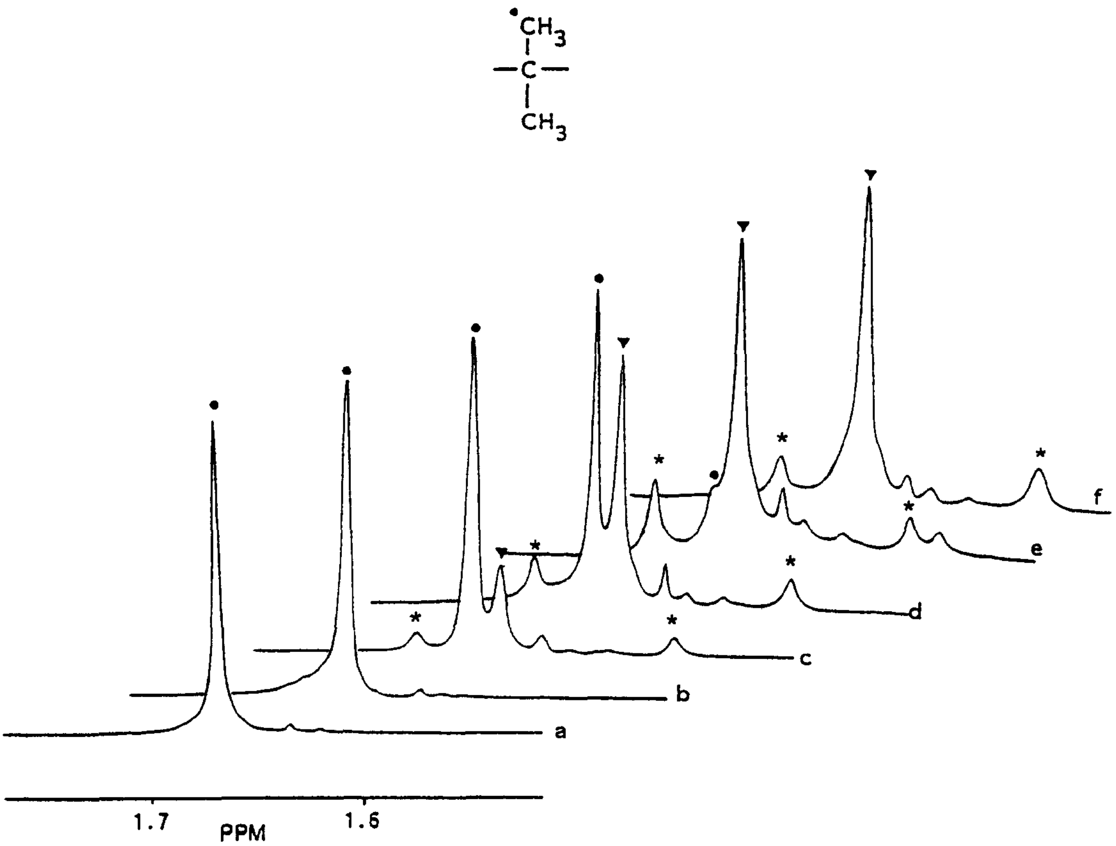


Fig. 5. Kinetics of CPCy at 230°C followed by ^{1}H-NMR (aliphatic protons). (●) CPCy; (▼) aryl cyanurate; and (*) intermediate products. a: t = 0 hr 15; b: t = 0 hr 30; c: t = 1 hr 00; d: t = 1 hr 30; e: t = 4 hr 00; and f: t = 5 hr 00.

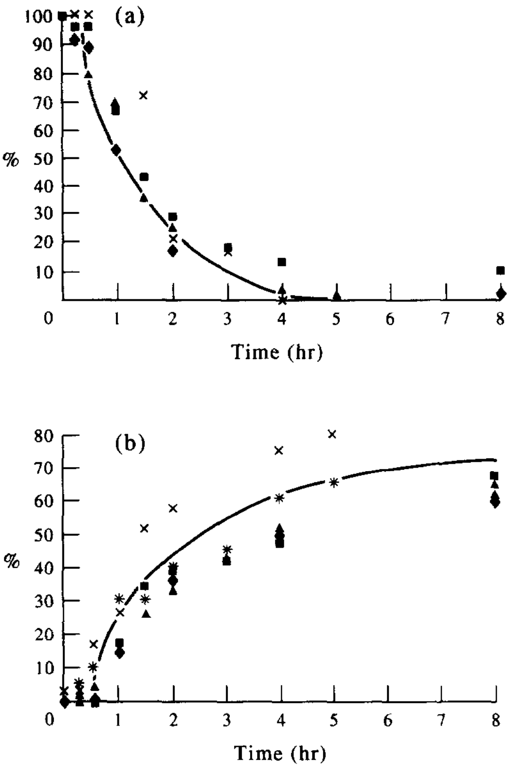


Fig. 6. Kinetics curves obtained for CPCy and aryl cyanurate. (a) CPCy: (◆) HPLC; (■) ^{1}H-NMR; (▲) ^{13}C-NMR; and (×) FTIR. (b) Aryl cyanurate for ^{1}H-NMR; (◆) HPLC; (■) ^{1}H-NMR (aliphatic protons); (▲) ^{1}H-NMR (aromatic protons); (×) ^{13}C-NMR; and (*) FTIR.

suggesting the presence of two or more different and successive reactions.

Changes in the polymerized reaction mixture (isothermal at 200°C) were followed by HPLC (Fig. 9). At zero time three peaks were present in the chromatogram, at respective retention volumes of 3, 9.5 and 24 ml. Based on the use of different standards, the first was attributed to PGE, the second the CPCy and the third to aryl cyanurate. Before the disappearance of PGE, peaks around 5, 16 and 18 ml appeared simultaneously. Figure 10 shows the evolution of new or residual species. In order to identify each peak, a 1/1 mixture was treated for 45 min at 250°C, subjected to preparative chromatography and each fraction was isolated and analyzed by ^{1}H- and ^{13}C-NMR, and by FTIR.

The ^{13}C- and ^{1}H-NMR chemical shifts of fraction 3 (Fig. 11 and Table 3) enabled the structure of the compound to be attributed to the formation of a four-membered ring corresponding to the intramolecular ring closure of two CPCy molecules according to the mechanism proposed in Fig. 12. It is to be noted that the chemical shifts of H_3 protons resonated around 6.7 ppm, signals that were also present in the spectra of CPCy homopolymerization (Fig. 5), confirming the mechanism in Fig. 12. The presence of a band around 1650 cm^{-1} in FTIR (oxazoline νO—C═N) refuted this structure (Fig. 13).

The FTIR spectra of fractions 4 and 5 contained a band around 1750–1740 cm^{-1}, characteristic of a carbonyl group, and an intense band towards 1237 cm^{-1}, characteristic of ether groups (Fig. 13). Published data [7, 8] are consistent with the presence of two substituted oxazolidinones arising from isocyanurate–epoxy reactions. The isocyanurate described by Bauer *et al.* [8, 9] was not isolated in this work, however, the epoxy–cyanate mechanisms were reconsidered. In the course of CPCy homopolymerization, a carbamate type reaction intermediate was detected. In light of earlier work in our laboratory [11], it was believed that it was the carbamate that reacted in the presence of epoxy. In order to confirm this, we synthesized CPCy carbamate as described [12] and investigated its reactions in the presence of PGE by FTIR and ^{13}C-NMR.

The FTIR results showed that the wave number of the carbamate alone νC═O was around 1710 cm^{-1}. In the presence of molten epoxy groups and at 180°C, three reactions were expected: epoxy group opening by primary and secondary amines, and epoxy group opening by hydroxyl groups [13]. The FTIR study of epoxy–carbamate reactions at different epoxy concentrations showed the presence of two bands around 1695 and 1739 cm^{-1}, the latter becoming predominant at an epoxy:carbamate ratio of 4.

The HPLC analysis of the same samples confirmed that the product is isolated in fraction 4 had the structure of a product arising from epoxy–carbamate reactions (Table 4). These results were corroborated by ^{13}C-NMR spectra: in particular, chemical shifts characteristic of epoxy group opening reactions by amine and hydroxyl groups were found in the 75–40 ppm region. The ^{13}C-NMR spectrum, however, could be interpreted only by the formation of an oxazolidinone ring. In an earlier study of epoxy–isocyanate reactions [14] we had isolated and identified the chemical shifts of these compounds (Table 5) which were the same as those in the spectrum of fraction 5. In order to attribute the different carbons, DEPT techniques were used enabling their class to be unambiguously determined (see as an example Fig. 14, the spectrum obtained for fraction 5).

The FTIR spectrum of fraction 6 contained two bands at 1566 and 1369 cm^{-1}, confirming the formation of aryl cyanate. The ^{13}C-NMR spectrum was identical to that observed in the homopolymerization of CPCy.

CONCLUSIONS

In the presence of pure CPCy and with no catalyst present, the formation of two reaction intermediates is difficult to explain since reactions were run in a dry atmosphere. We nevertheless believe that traces of water catalyzed the system, as depicted in Fig. 12. Based on the chemical shifts of CPCy carbamate and monophenol, we were able to detect their presence in the reaction mixture. On the other hand, the lines of the four-membered ring intermediate could be attributed on the basis of epoxy–cyanate results, since it was isolated and characterized by ^{1}H- and ^{13}C-NMR.

These data were confirmed by the kinetics of the PGE:CPCy (1:1) reaction mixture, followed by FTIR, NMR and HPLC. Since no epoxy groups were

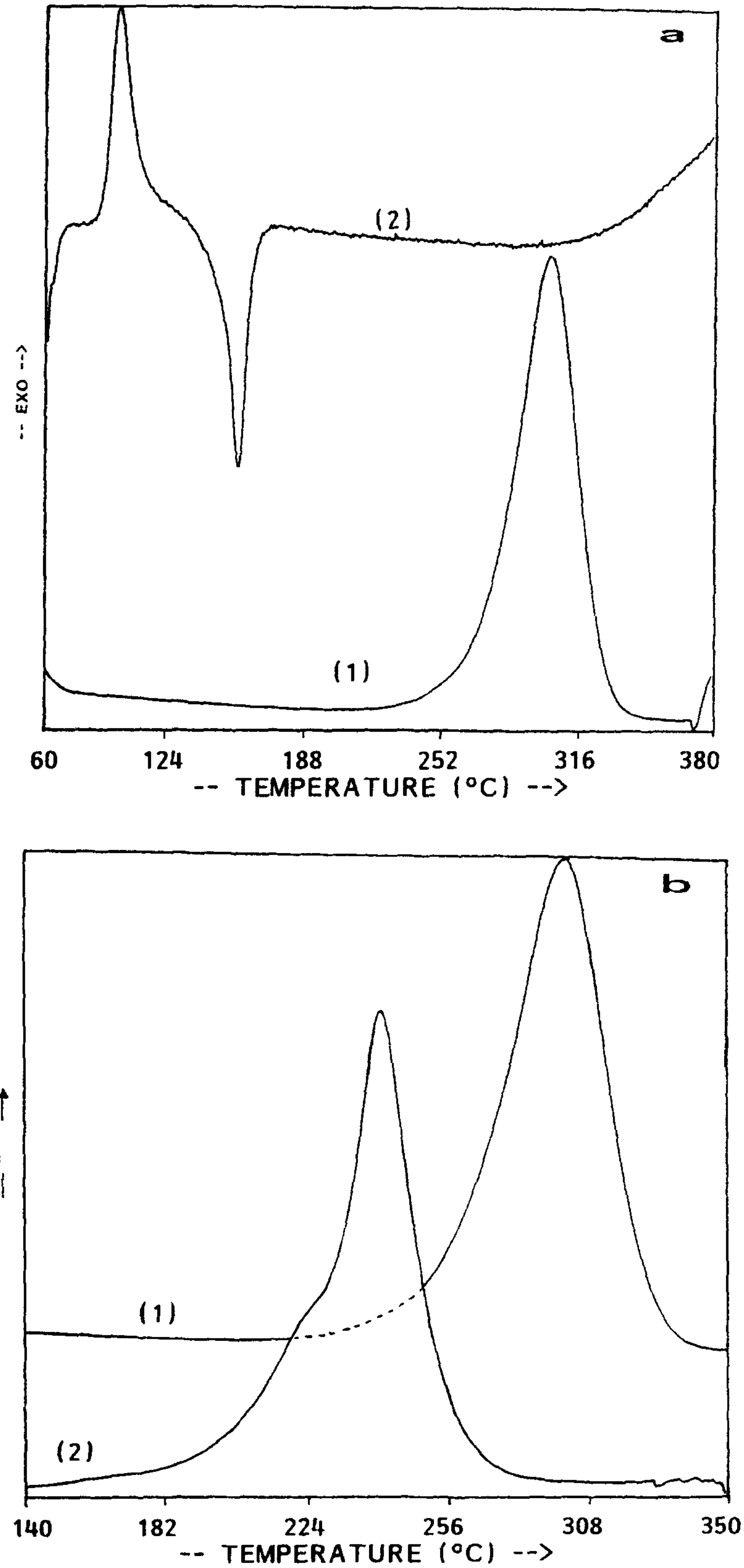


Fig. 7. a: Dynamic DSC thermal diagrams from 60 to 380°C (5°C/min). (1) CPCy alone and (2) CPCy advanced for 24 hr at 230°C containing 60% aryl cyanurate and 40% secondary products in the reaction mixture. b: Dynamic DSC thermal diagrams. (1) CPCy alone; and (2) CPCy/PGE (1/1).

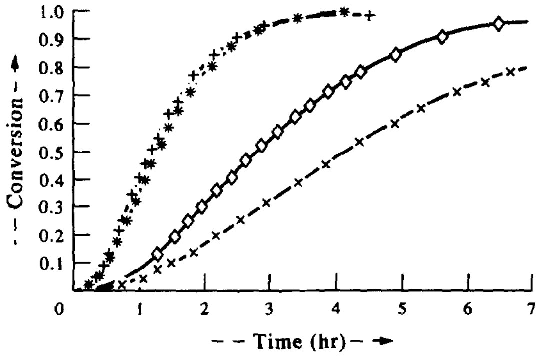


Fig. 8. Kinetics curves of CPCy obtained by isothermal calorimetry: (×) 200°C; (◇) 205°C; (+) 210°C; and (*) 220°C.

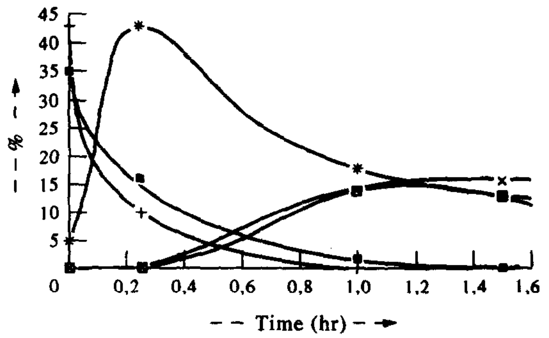


Fig. 10. Quantization of the chemical species in the CPCy/PGE system at 250°C by HPLC: (■) PGE; (+) CPCy; (*) aryl cyanurate; (□) fraction 3; and (×) fraction 5.

present, all the chemical species described had to be present in the reaction mixture. This was observed with FTIR, since wave numbers at 1750, 1738, 1695, 1566 and 1364 cm^{-1} were found, corresponding to the different fractions previously isolated and studied. In addition, HPLC confirmed that the homopolymerization of cyanate groups occurred first, followed by reaction with the epoxy and hydroxyl groups formed. Similarly, ^{13}C-NMR (Table 6) showed that all the chemical species identified in the study of the different fractions were found in the medium. These results confirm that the reaction mechanism of epoxy–cyanate system is complex and depends on the amount of each component.

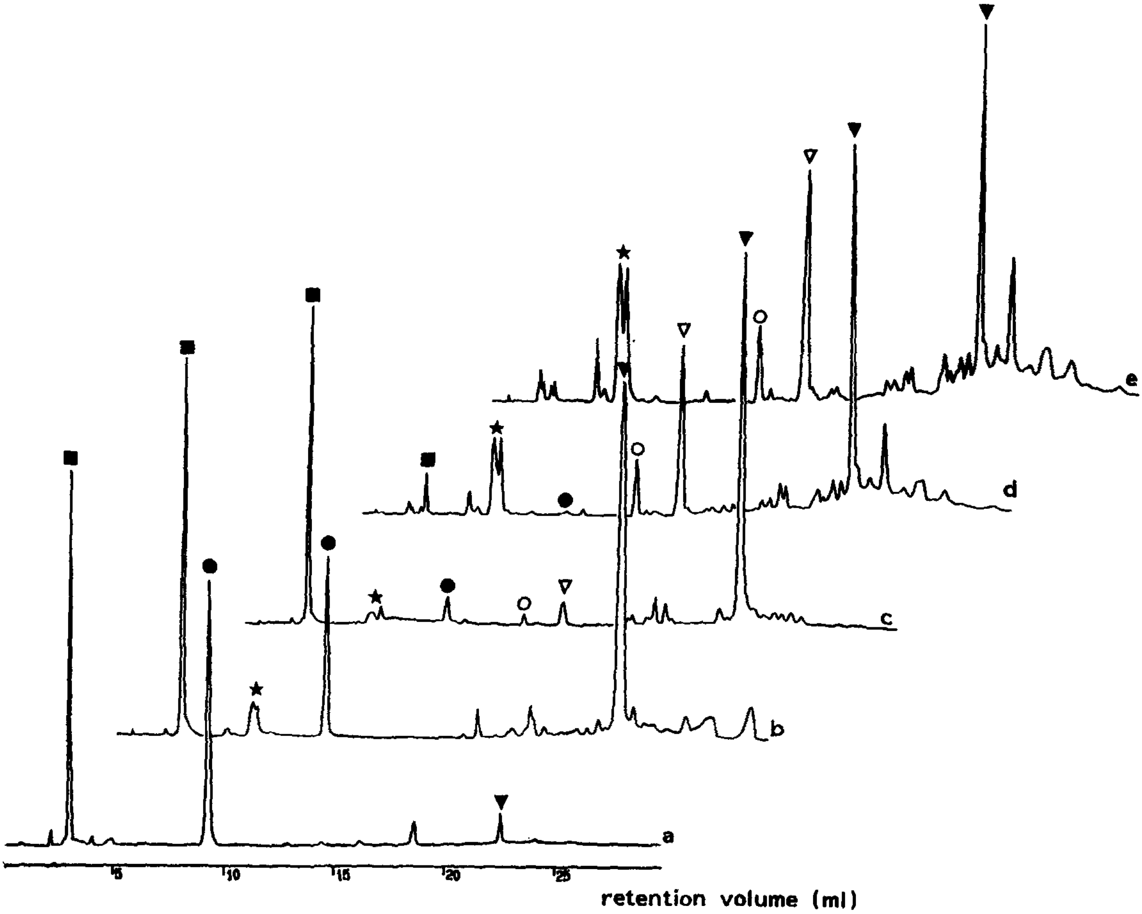


Fig. 9. Kinetics of CPCy/PGE copolymerization followed by HPLC: (■) fraction 1; (●) fraction 2; (★) fraction 3; (○) fraction 4; (▽) fraction 5; and (▼) fraction 6. a: $t = 0$; b: $t = 0$ hr 15; c: $t = 0$ hr 30; d: $t = 1$ hr 00; and e: t 1 hr 30.

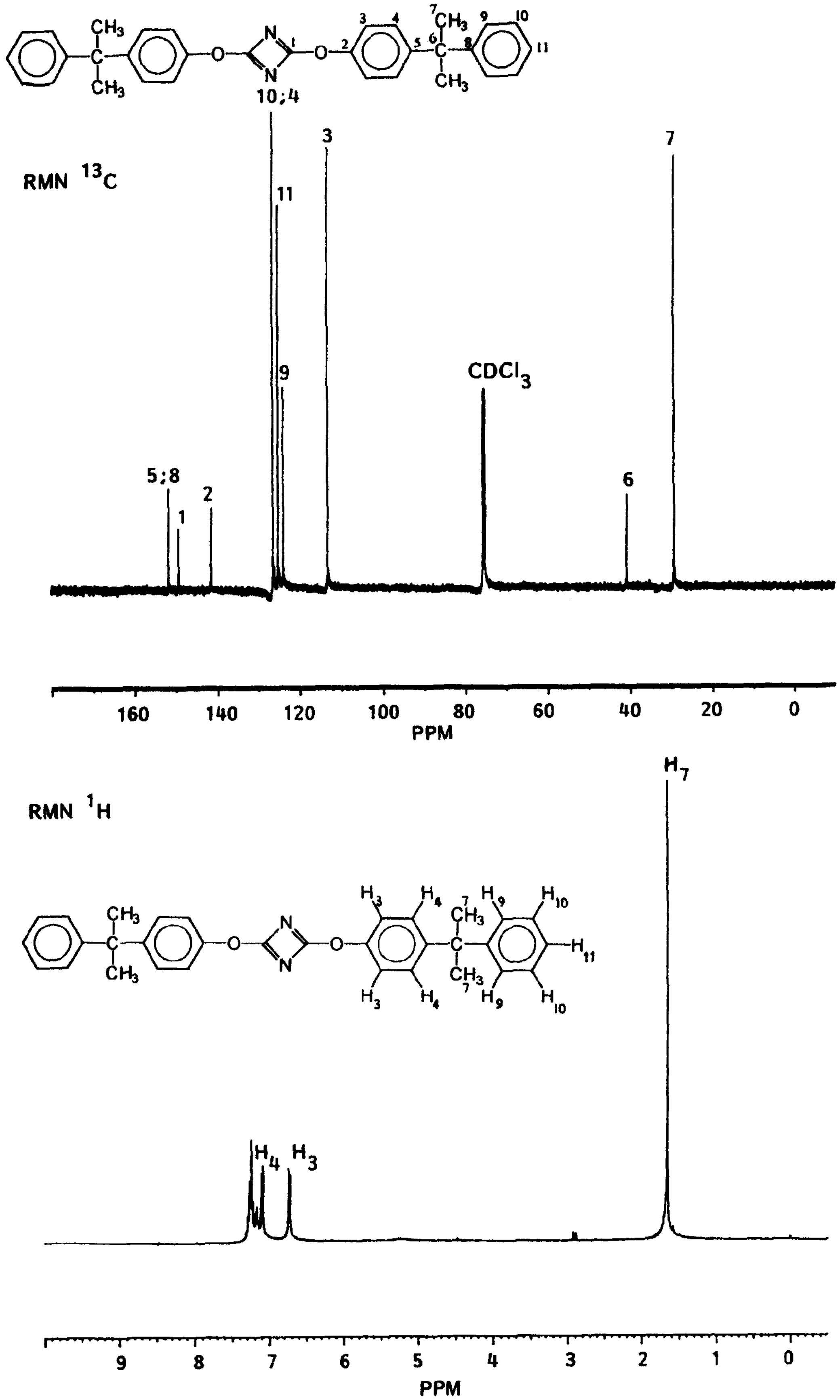


Fig. 11. ^1H- and ^{13}C-NMR spectra of fraction 3.

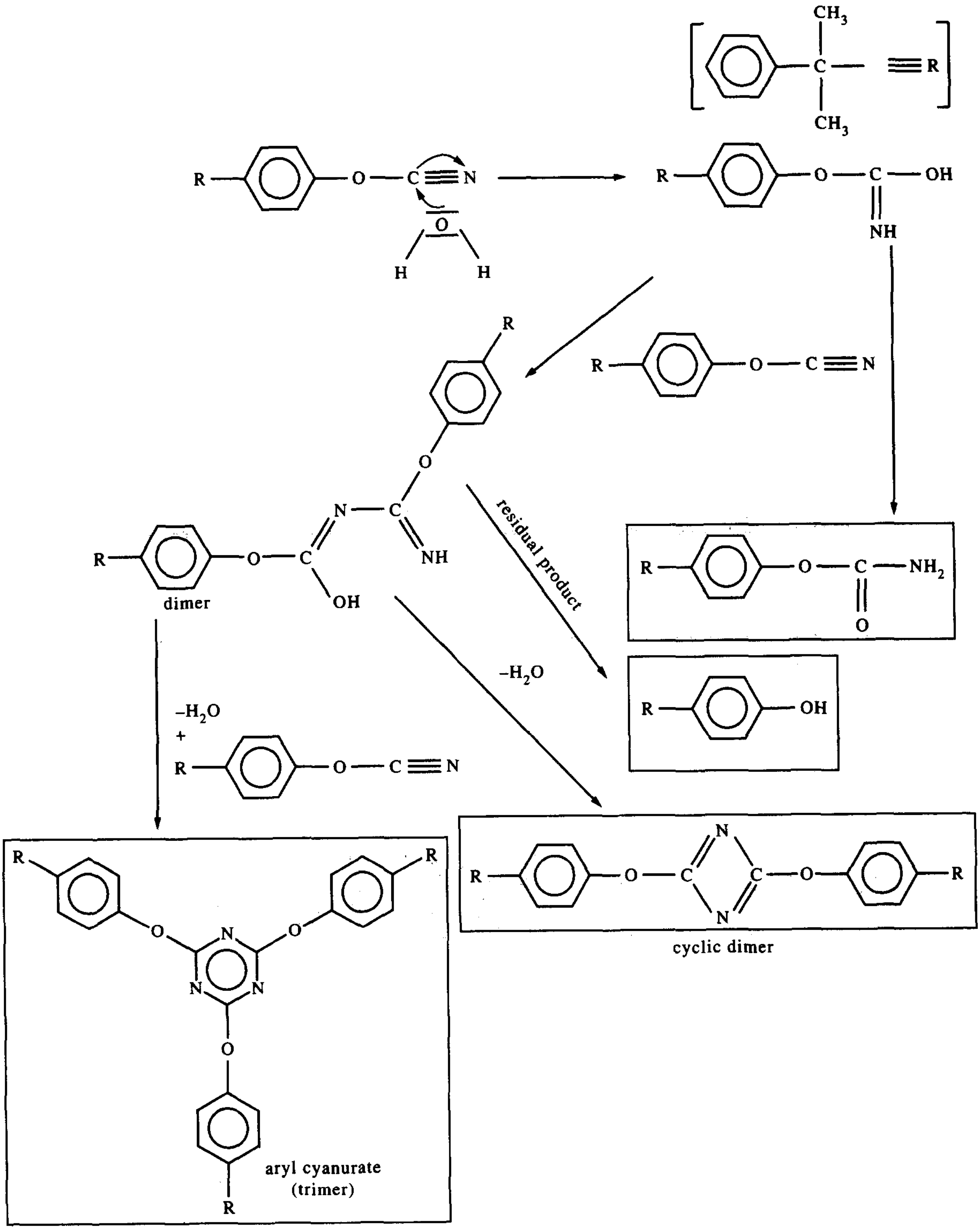


Fig. 12. Homopolymerization reaction path.

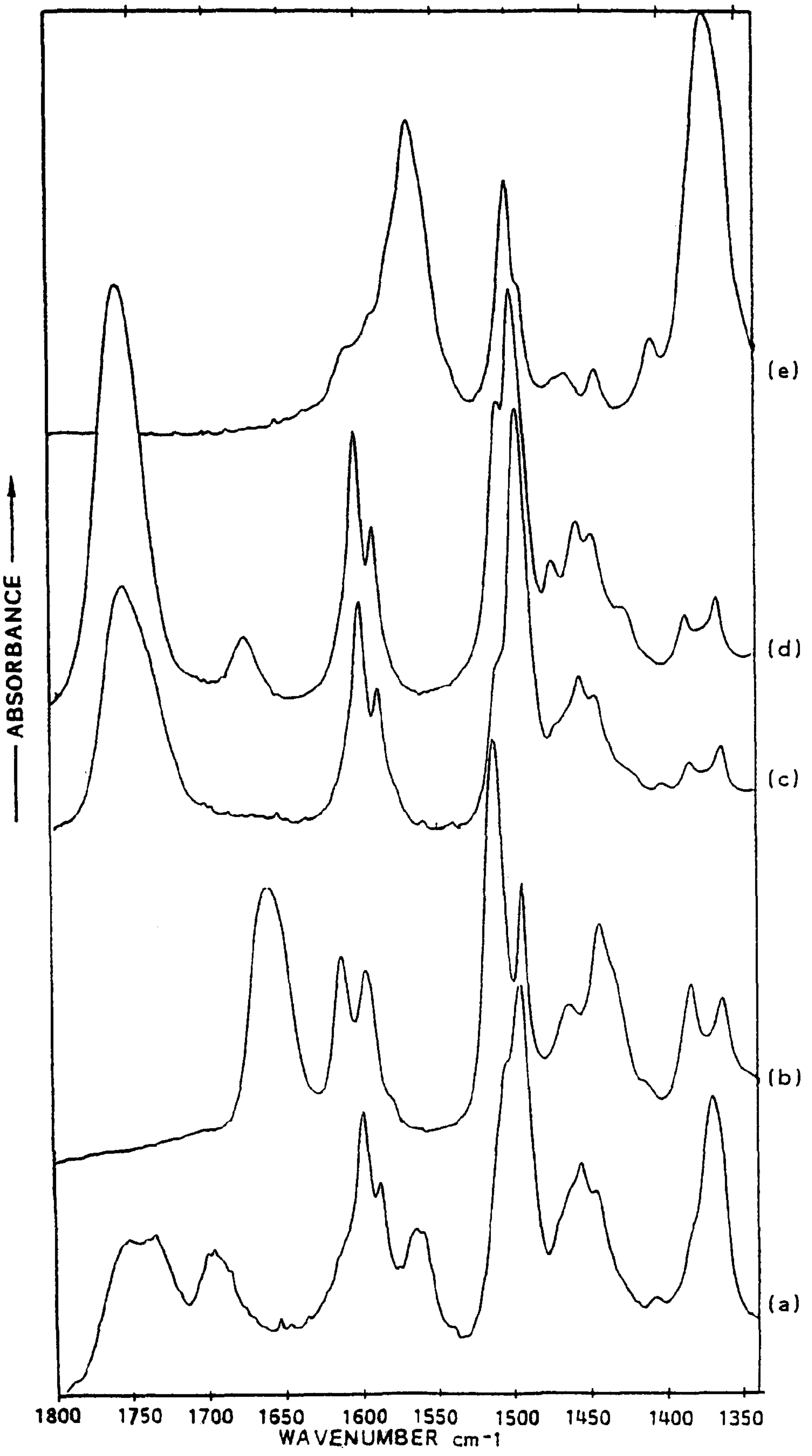
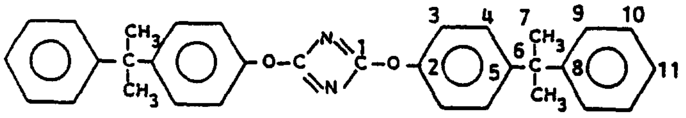


Fig. 13. FTIR spectra (1800–1340 cm^{-1}) of the fractions obtained after separation of the CPCy/PGE (1/1) mixture treated at 250°C for 45 min. (a) CPCy/PGE 250°C 45 min; (b) fraction 3; (c) fraction 4; (d) fraction 5; and (e) fraction 6.

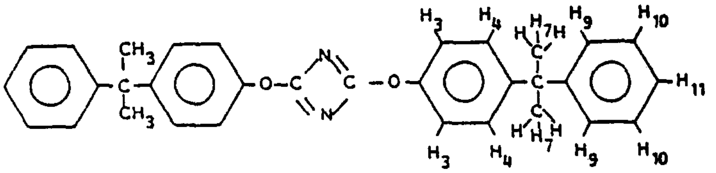
Table 3. ^{1}H- and ^{13}C-NMR chemical shifts of fraction 3

RMN ^{13}C



carbons	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}
δ (PPM)	149.3_3	141.5_6	113.1_8	126.4_2	151.7_2	40.7_2	29.3_1	151.7_2	123.9_7	126.4_2	125.1_5

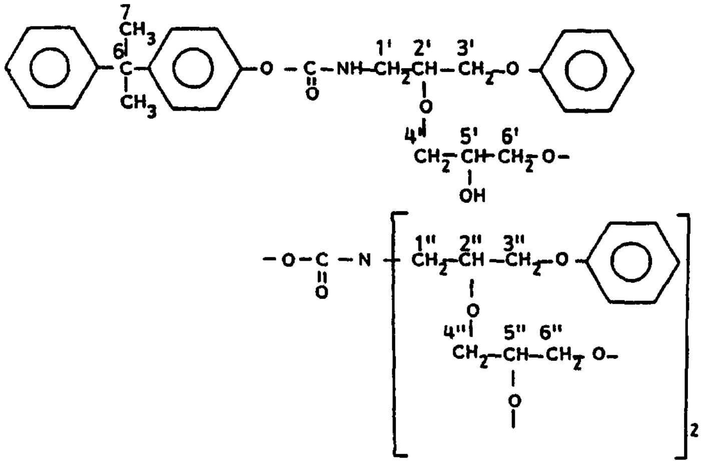
RMN ^{1}H



protons	H_3	H_4	H_7	H_9	H_{10}	H_{11}
δ (PPM)	6.7_2	7.1_0	1.6_4	7.2_3	7.2_5	7.1_6

Table 4. ^{13}C-NMR chemical shifts (75–30 ppm region) of the cumyl carbamate/PGE system

δ (PPM)	(2:1)	δ (PPM)	(1:1)
74.2_5	4'	74.4_5	4"
69.5_4	6'	69.2_5	6"
69.41	2'	68.8_1	2"
68.7_7	3'	68.5_2	3"
68.0_5	5'	68.4_9	5"
46.0_1	1'	67.9_4	1"
42.3_2	6	67.6_5	1"
30.8_8	7		



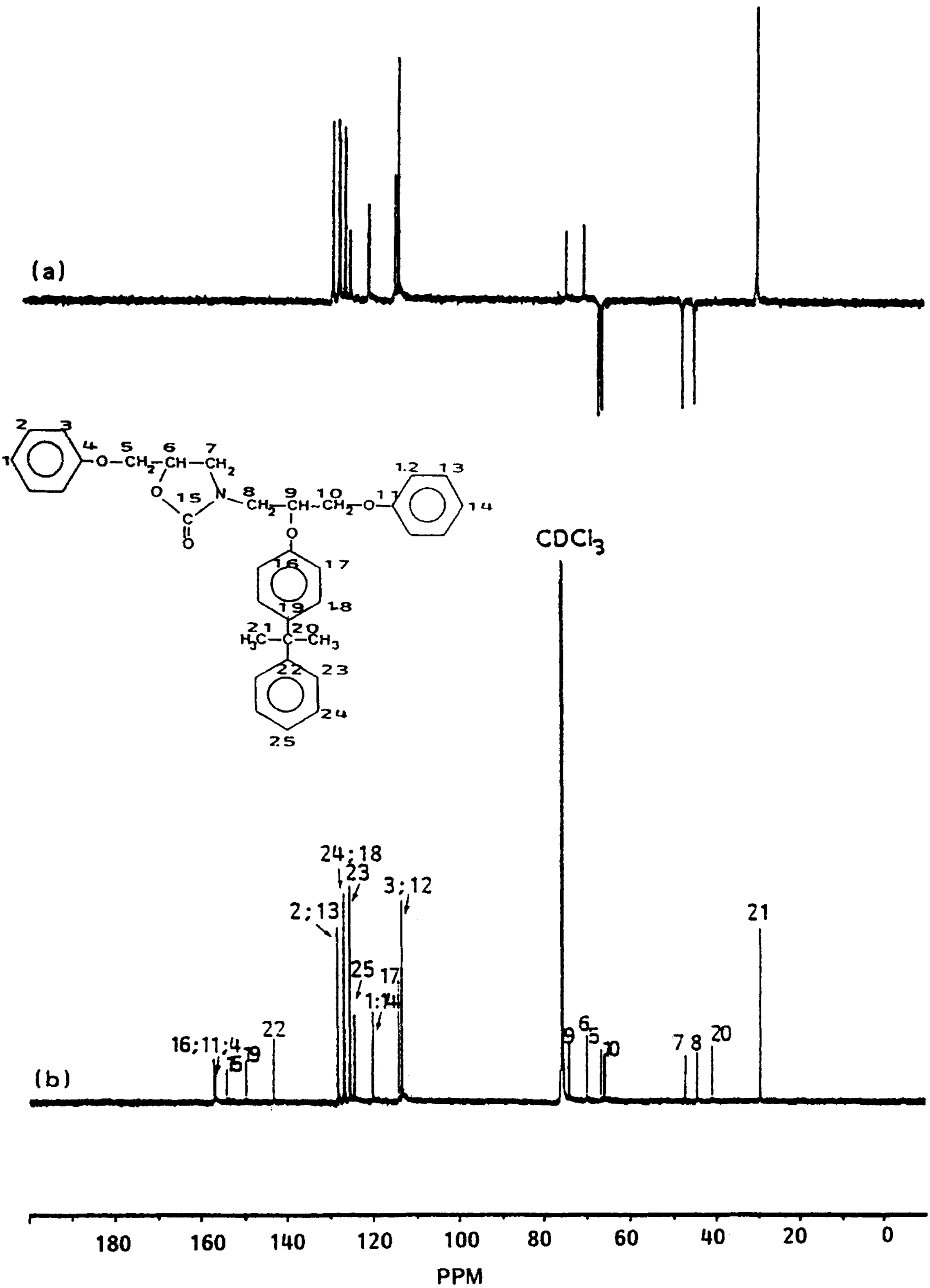


Fig. 14. ^{13}C-NMR spectrum of fraction 5. (a) Spectrum before DEPT pulse sequence; (b) Spectrum after DEPT pulse sequence.

Table 5. ^{13}C-NMR chemical shifts of fraction 5

carbons	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
δ (PPM)	121.9_5	129.9_5	114.9_7	158.2_2	68.3_5	71.6_3	49.0_2	46.2_6	75.7_5	67.5_3	158.4_1	114.9_7
C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}
129.9_5	121.7_3	155.5_8	158.7_1	115.8_2	128.4_6	151.0_1	42.7_6	31.2_3	144.6_7	127.1_0	128.4_7	126.0_3

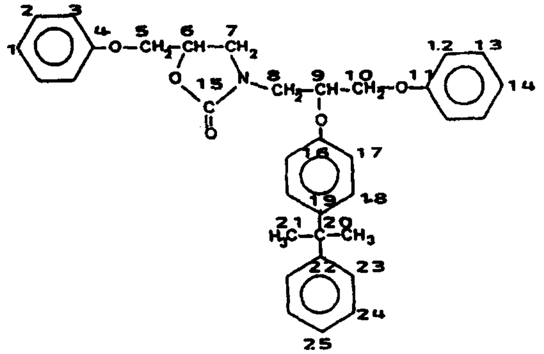


Table 6. Attribution of ^{13}C-NMR lines specific to fractions 3–6 in the CPCy/PGE (1/1) reaction mix, 250°C 45 min

δ (PPM)	173.5	158.4–158.0	155.1	151.7	151.1	150.1	149.3	148.4
assignment	C_1 aryl cyanurate (no. 6)	quaternery carbons of oxazolidinone (no. 5)	C=O of oxazolidinone (no. 5)	quaternery carbons (no. 3)	—C≡N (no. 3)	C_8 aryl cyanurate (no. 6)	C_2 aryl cyanurate (no. 6)	C_5 aryl cyanurate (no. 6)
δ (PPM)	144.3	74.1	71.3	69.4	68.1	67.9–67.0	42.4–42.2	30.8
assignment	quaternery carbons of oxazolidinone (no. 5)	—C—O homopolymérization (no. 3)	—CH— of oxazolidinone (no. 5)	—CH—O— (no. 4)	—CH—OH— (no. 4)	CH—CH_2—O— of oxazolidinone (no. 5)	—C—	—CH_3

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REFERENCES

1. D. Martin. *Angew. Chem.* **76,** 303 (1964).
2. J. T. Gotro, B. K. Appelt and K. I. Papathomas. *Polym. Comp.* **8,** 39 (1987).
3. D. A. Shimp, F. A. Hudock and S. J. Ising. *Sampe Int. Symp.* **33,** 754 (1988).
4. M. Bauer, J. Bauer, R. Ruhmann and G. Kuhn. *Acta Polymer.* **40,** 6 and 397 (1989).
5. M. Bauer, W. Tanzer, H. Much and R. Ruhmann. *Acta Polymer.* **40,** 5 and 335 (1989).
6. J. Bauer and M. Bauer. *J. Macromol. Sci.—Chem. A* **27,** 97 (1990).
7. D. A. Shimp and J. E. Wentworth. *Sampe Int. Symp.* **38,** 292 (1992).
8. M. Bauer, J. Bauer and G. Kuhn. *Acta Polymer.* **37,** 11 (1986).
9. J. Bauer and M. Bauer. *Acta Polymer.* **38,** 12 (1987).
10. O. Georjon, J. Galy and J. P. Pascault. *J. Appl. Polym. Sci.* **49,** 1441 (1993).
11. M. F. Grenier-Loustalot, M. P. Bente and P. Grenier. *Europ. Polym. J.* **31,** 3049 (1993).
12. N. Rabjohn. *Organ. Synth.* **4,** 760 (1963).
13. M. F. Grenier-Loustalot, P. Grenier and M. P. Bente. *Europ. Polym. J.* **28,** 987 (1992).
14. D. Caille, L. Tigzert, J. P. Pascault, M. F. Grenier-Loustalot and P. Grenier. *Polym. Netw. Blends* **3,** 183 (1993).