

# NOTES

## Ionic Polymeric Peroxycarbamates

There has been growing interest in the synthesis of cationic polyurethanes because of their high electric conductivity. Some cationic polyurethanes were synthesized by the Menshutkin reaction.<sup>1,2</sup> Alternatively, direct polyaddition reaction between a macrodiisocyanate and some diol or diamine compounds yields polyurethanes with tertiary nitrogen atoms that are capable of a subsequent quarternization reaction.<sup>3</sup> The resulting polyurethane represents properties of both rigid polycation segment and flexible polyether segment.

Peroxycarbamates (PC) are synthesized by utilizing well-established techniques of polyurethane chemistry. The polymeric and dimeric PCs were used as free radical initiators in the polymerization and block copolymerization of vinyl monomers.<sup>4-6</sup> Block copolymerization is a two-step procedure and involves the sequential decomposition of peroxy linkages that are introduced in the initiator. We have recently extended this procedure to cation susceptible monomers, such as butylvinylether.<sup>7</sup> In these processes, macroradicals, obtained by the thermolysis of polymeric peroxycarbamates or polymers having residual bonds, are converted to carbocations by the use of iodonium or silver salts.

In this study, we describe the synthesis of new cationic polymeric peroxycarbamates (CPPC) having appropriate functionality for subsequent vinyl polymerization. Dilute solution behavior of CPPPs in DMF was also studied.

### RESULTS AND DISCUSSION

CPPCs were prepared using a general procedure of polyurethane chemistry. First, 1,4-butanediol and luperox-2,5-2,5 were end-capped with 2,4-Toluene diisocyanate (TDI) and 3-isocyanatomethyl-3,5,5-trimethyl cyclohexyl isocyanate (IPDI), respectively. Cycloaliphatic isocyanate was deliberately employed, since attempts to end-cap the dihydroperoxide with TDI resulted in chain extension and formation of insoluble material. Furthermore, we have recently shown<sup>8</sup> that polymeric peroxycarbamate, having a

substituted cyclohexyl moiety, was an effective initiator for vinyl polymerization with negligible transfer to the initiator. Subsequently, these molecules with isocyanate end groups were extended with *N,N'*-bis ( $\beta$ -hydroxyethyl)-piperazine. The chain extension reaction was conducted at room temperature in order to prevent the thermal scission of the peroxygen bonds. At this step, dibutyltin dilaurate (T-12) was added as a catalyst, which caused a significant increase in the reaction rate. Special care was taken for the removal of unreacted material from the product. IR spectroscopy was routinely used to follow the reactions by monitoring the disappearance of the NCO and OH bands at around 2250 and 3520  $\text{cm}^{-1}$ , and to monitor and appearance of (NH) and (C=O) absorptions at around 3440 and 1730  $\text{cm}^{-1}$ , respectively. The tertiary nitrogen atoms were then quarternized with methyl iodide. The overall synthetic procedure is represented in Scheme 1. It is evident that one equivalent of the tertiary amine groups theoretically corresponds to two equivalents of the urethane groups. Synthetic and structural characteristics of CPPCs are shown in Tables I and II. A quarternization degree of 79.42–96.28 was achieved by using an excess of methyl iodide.

The CPPCs obtained form transparent, but brittle, films, which adhere to glass, metal, and wood. Similarly, films cast from cationic polyurethanes, which have only hard segments, became easily friable after drying.<sup>9</sup>

The CPPCs have good hydrophilicity because of the presence of electrical charges on the macromolecular chain. As shown in Table III, increasing concentration of Luperox 2,5-2,5 groups improves the hydrophilic character of CPPC. This behavior may be attributed to the peroxy groups present in the structure, which are potential sites for hydrogen bridges with water.

The behavior of dilute solutions of CPPCs in a polar solvent, such as DMF, was also studied. As a result of the ionization of the ionic groups in CPPCs, the dilute solutions in DMF behave in a similar fashion as compared with aqueous polyelectrolyte solutions. Viscosity of the solutions increases markedly by reducing polymer concentration, which is the characteristic behavior for polyelectrolytes (Fig. 1). Polyelectrolyte behavior was destroyed by adding 1  $\text{mol L}^{-1}$  potassium iodide in DMF diluted solutions of CPPCs. The reduced viscosity did not increase by dilution, probably because the ionic interac-

**Table I Synthesis of Cationic Polymeric Peroxycarbamates**

| Cationic<br>Polymeric<br>Peroxycarbamate | IPDI—Luperox—IPDI<br>(mmol) | TDI—BD—TDI<br>(mmol) | IPDI—Luperox—IPDI<br>+ TDI—BD—TDI<br>(mol ratio) |   | BHEP<br>(mmol) | Yield<br>(%) | $\bar{M}_n^a$ |
|--|-----------------------------|----------------------|--|---|----------------|--------------|---------------|
|  |                             |                      |  |   |                |              |               |
| CPPC-1                                   | —                           | 4                    | —  | — | 4              | 85.0         | 2850          |
| CPPC-2                                   | 1                           | 4                    | 0.20   | — | 5              | 88.5         | 4025          |
| CPPC-3                                   | 1                           | 3                    | 0.25   | — | 4              | 81.6         | 3850          |
| CPPC-4                                   | 2                           | 2                    | 0.50   | — | 4              | 72.2         | 4275          |
| CPPC-5                                   | 4                           | —                    | 1.00   | — | 4              | 63.0         | 3205          |

<sup>a</sup> Determined by cryoscopy in DMSO.

**Table II The Structural Characteristics of Cationic Polymeric Peroxycarbamates**

| Cationic<br>Polymeric<br>Peroxycarbamate | Peroxygen Content<br>meq/100 g | Urethane Groups <sup>a</sup><br>meq/100 g | Ionic Iodine Content<br>meq/100 g |            | Quarternization<br>Degree (%) |
|--|--------------------------------|---|-----------------------------------|------------|-------------------------------|
|  |                                |   | Found                             | Calculated |                               |
| CPPC-1                                   | —                              | 292.96                                    | 146.48                            | 184.46     | 79.42                         |
| CPPC-2                                   | 66.25                          | 358.30                                    | 147.74                            | 179.14     | 81.85                         |
| CPPC-3                                   | 85.00                          | 355.80                                    | 146.64                            | 177.87     | 82.42                         |
| CPPC-4                                   | 113.75                         | 343.80                                    | 155.62                            | 171.90     | 89.94                         |
| CPPC-5                                   | 307.50                         | 322.28                                    | 154.60                            | 161.14     | 96.28                         |

<sup>a</sup> Theoretical value.

tions were screened by the diffusion of the salt in the polymerization (Fig. 2).

In conclusion, this synthetic procedure leads to a polymeric peroxycarbamate with —O—O— groups and electrically

charged nitrogen atoms in the main chain. Polymeric product functionalized in this way will decompose upon heating and will form radicals in a similar way as peroxides.

If the thermolysis is carried out in the presence vinyl-type monomers, radicals having ionic segments may initiate free radical polymerization to generate copolymers. Detailed studies in this line are now in progress and the results will be reported elsewhere.

**Table III Moisture Content of Film from Cationic Polymeric Peroxycarbamates**

| Cationic<br>Polymeric<br>Peroxycarbamate <sup>a</sup> | Ionic Iodine<br>Content<br>meq/100 g | Moisture Content<br>at RH = 85%<br>(%) |
|---|--------------------------------------|--|
| CPPC-1  | 146.68                               | 6.90                                   |
| CPPC-2  | 147.74                               | 6.50                                   |
| CPPC-3  | 146.64                               | 6.85                                   |
| CPPC-4  | 155.62                               | 8.50                                   |
| CPPC-5  | 154.60                               | 7.70                                   |

<sup>a</sup> Thickness of film: 0.50–0.75 mm.

## EXPERIMENTAL

### Materials

3-Isocyanatomethyl-3,5,5-trimethyl cyclohexyl isocyanate (IPDI), 2,4 Toluene diisocyanate (TDI) were products of Fluka A.G. and their purities were determined by isocyanate analysis.

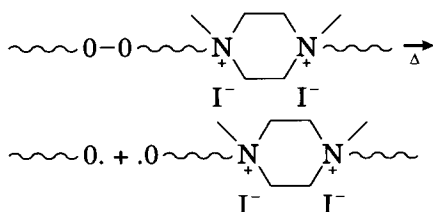
2,5-Dimethyl-2,5 dihydroperoxyhexane, (Luperox-2,5-2,5,Luperox) was supplied by Lucidol Division, Penwalt Corp. It was recrystallized from carbon tetrachloride. The peroxygen content was 98% of the theoretical value.

1,4-Butanediol (BD) (Merck A.G.) and *N,N'*-bis ( $\beta$ -hydroxyethyl)-piperazine (BHEP) (Aldrich) were dried under vacuum before use.

Methyl iodide (Aldrich) and Dibutyltin dilaurate (Carstan DBTDL, T-12) (Fluka A.G.) were used without further purification.

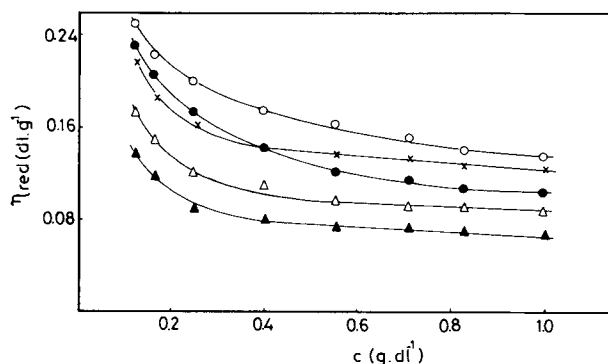
All solvents were purified according to conventional drying and distillation procedures.

**Preparation of CPPCs.** For the synthesis of CPPCs, isocyanate end-capped compounds were prepared as starting materials according to the following procedures (See Scheme 1 for the synthetic steps):

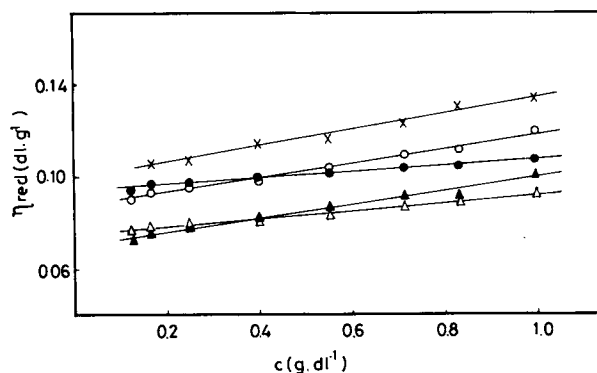


Scheme 1

**IPDI—Luperox—IPDI.** 15 mmol Luperox-2,5-2,5 and 45 mmol IPDI were reacted in 40 mL of dichloroethane in the presence of T-12 catalyst (0.06 g) at room temperature under dry nitrogen atmosphere in the dark for 80 h. The product was precipitated into 250 mL dry petroleum ether and filtered, washed, and dried in a vacuum oven at room temperature. Yield was 65.1% and peroxygen content 8.22%. Isocyanate content was 10.71% and  $M$  (from the



**Figure 1** Plot of viscosity number against concentration of solutions in DMF for cationic polymeric peroxy-carbamates. (×): CPPC-1, (○): CPPC-2, (●): CPPC-3, (Δ): CPPC-4, (▲): CPPC-5.



**Figure 2** Plot of viscosity number against concentration of solutions in DMF with 1 mol potassium iodide/l for cationic polymeric peroxy-carbamates. (×): CPPC-1, (○): CPPC-2, (●): CPPC-3, (Δ): CPPC-4, (▲): CPPC-5.

peroxygen content) was  $778.6 \text{ g mol}^{-1}$ . The  $M$  (from isocyanate content) was  $784.3 \text{ g mol}^{-1}$ .

**TDI—BD—TDI.** 20 mmol BD and 60 mmol TDI were reacted in 40 mL of THF at  $60^\circ\text{C}$  under nitrogen atmosphere for 60 h. At the end of this period, the mixture was poured into 200 mL of dry petroleum ether, purified, and finally was dried in a vacuum oven at  $50^\circ\text{C}$ . Yield was 86.8%, isocyanate content was 13.4%, and  $M$  (from isocyanate content) was  $627 \text{ g mol}^{-1}$ .

**Preparation of CPPCs.** Appropriate solutions of purified IPDI—Luperox—IPDI, TDI—BD—TDI, and BHEP in 25 mL DMF were reacted in the presence of T-12 catalyst (0.06 g) at  $40^\circ\text{C}$  under nitrogen atmosphere in the dark for 80 h. All polymeric products were then precipitated into diethyl ether and were dried. Subsequently, the polymeric peroxy-carbamates obtained were dissolved in 25 mL of DMF and were treated with excess methyl iodide at room temperature for 24 h. Finally, the cationic polymeric peroxy-carbamates were purified as described above.

## ANALYSIS

Isocyanate and peroxygen content were determined as described previously.<sup>8</sup> The iodine content was determined titrimetrically by the Volhard method. The viscosity was measured with an Ubbelohde viscometer with OA capillary at  $30 \pm 0.2^\circ\text{C}$  using freshly distilled DMF.

The films were obtained from DMF/ $\text{CH}_3\text{OH}$ , 90/10 (v/v) solutions by evaporation on a teflon surface.

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