

Ring-Opening Polymerization of ϵ -Caprolactone by Iodine Charge-Transfer Complex

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ABSTRACT: The ring-opening polymerization of ϵ -caprolactone (ϵ -CL) catalyzed by iodine (I_2) was studied. The formation of a charge-transfer complex (CTC) among triiodide, I_3^- , and ϵ -CL was confirmed with ultraviolet–visible spectroscopy. The monomer ϵ -CL was polymerized in bulk using I_2 as a catalyst to form the polyester having apparent weight-average molecular weights of 35,900 and 45,500 at polymerization temperatures of 25 and 70 °C, respectively. The reactivity of both, ϵ -CL monomer and ϵ -CL: I_2 CTC, was interpreted by means of the potential energy surfaces determined by semiempirical computations (MNDO-d). The results suggest that the formation of the ϵ -CL: I_2 CTC leads to the ring opening of the ϵ -CL structure with the lactone protonation and the formation of a highly polarized polymerization precursor (ϵ -CL)⁺. The band gaps approximated from an extrapolation of the oligomeric polycaprolactone (PCL) structures were computed. With semiempirical quantum chemical calculations, geometries and charge distributions of the protonated polymerization precursor (ϵ -CL)⁺ were obtained. The calculated band gap (highest occupied molecular orbit/lowest unoccupied molecular orbit differences) agrees with the experiment. The analysis of the oligomeric PCL isosurfaces indicate the existence of a weakly lone pair character of the C=O and C—O bonds suggesting a ϵ -CL ring-opening specificity. © 2002 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 40: 714–722, 2002

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INTRODUCTION

Polycaprolactone (PCL) is a linear polyester with a hydrophobic character as a result of the presence of five nonpolar methylene groups and a single relatively polar ester group in each repeating unit. It has been subject to intensive research

and development of biorresorbable polymeric formulations for use in orthopedic implants and drug delivery systems because of their biocompatibility and biodegradability properties as well as the retention of mechanical properties over an adequate period of time after implantation.^{1–7}

The polyester PCL is synthesized by the ring-opening polymerization of the cyclic ester ϵ -caprolactone (ϵ -CL). Several types of catalysts—acid, base, ionic, coordination, and enzymatic—have been developed for the ring-opening polymerization of ϵ -CL.^{8–12} Most notable and well-docu-

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mented among these catalysts are metal halides, metal alkoxides, and bimetallic μ -oxoalkoxides.¹³ Recently, the application of new initiators on the basis of the lanthanide elements for the ring-opening polymerization of ϵ -CL has markedly improved the potential for producing engineered PCL.¹⁴

Studies on the initiated the iodine polymerization of various vinyl monomers and some unsaturated five-membered heterocycle compounds that form high molecular weight polymers have been reported by several researchers.^{15–24}

Despite all these studies on the use of iodine as a polymerization catalyst, no one until now has reported that iodine is also able to promote the polymerization of cyclic lactones to produce polyesters similar to what we have discovered.

In this article, we report on the ring-opening polymerization of the ϵ -CL monomer by iodine for the first time, and a preliminary study of the electronic and conformational analysis of the reactive species by semiempirical MNDO-d calculations is presented.

MATERIALS AND METHODS

The monomer ϵ -CL obtained from Aldrich was dried with CaH_2 for 24 h and then distilled under reduced pressure. Iodine was purchased from Merck and purified by sublimation.

Iodine-induced ϵ -CL polymerization was carried out in bulk with septum-stoppered flasks in a bath, which was protected from light. The reaction temperature was controlled by an immersion cooler. A stoichiometric amount of pulverized iodine (sublimed, Merck) was added directly with vigorous agitation into ϵ -CL under N_2 . Reaction time was taken to start at the moment when the iodine was added. Afterward, the reaction mixture was precipitated with a large excess of cold ethanol. The resulting polymer was washed with 5% aqueous sodium thiosulfate solution for several times, distilled water, and dried over anhydrous sodium sulfate at room temperature under vacuum.

The obtained poly(ϵ -CL) was characterized by gel permeation chromatography (GPC), Fourier transform infrared (FTIR), and ^1H NMR spectroscopies. Molecular weight distributions were determined with a PerkinElmer GPC equipped with a refractive-index detector series 200. A set of 104-, 103-, and 500-Å PL-gel columns conditioned at 25 °C were used to elude the samples of 10

mg/mL concentration at a 1 mL/min high-pressure liquid chromatographic grade chloroform flow rate.

The weight-average (M_w) and number-average (M_n) molecular weights were determined using a calibration curve with polystyrene standards. The polydispersity index was calculated as the M_w/M_n ratio. Ultraviolet–visible (UV–vis) spectra were taken on a Beckman DU-50 spectrophotometer.

A Varian Unity-400 NMR spectrometer was used for all NMR experiments described herein. ^1H NMR spectra were recorded at 400 MHz. Chemical shifts in parts per million were reported downfield from 0.00 ppm using tetramethylsilane as the internal reference.

The semiempirical calculations reported in this article were performed using the MNDO-d model inside of the TITAN 1.05 suite of programs, which provides a state-of-the-art package for *ab initio* calculations. The procedure adopted in this work was as follows. Preliminary ϵ -CL monomeric structures were obtained by direct minimization of the total energies in classical molecular mechanic methods with respect to all geometric variables, that is, bond lengths and angles.^{25–30} Where necessary, several starting structures were used to achieve convergence. These structures were then refined by successive reoptimization of the geometry using MNDO-d basis sets, except where intractable convergence difficulties were encountered or the system was too large for our computational resources. The output includes the optimized geometry, molecular orbital energies (eigenvalues), and total electronic energy as well as orbital population.

RESULTS AND DISCUSSION

Recently, the iodine charge-transfer complexes (CTCs) have gained synthetic and mechanistic significance as a result of their potential applications in organic synthesis and development of novel materials.^{31–36}

To understand the interaction between iodine and ϵ -CL, the electronic spectra of iodine in CHCl_3 were recorded. Figure 1 shows a series of UV–vis absorption spectra of the ϵ -CL: I_2 complex. The absorption band due to free iodine appears at 502 nm without any additional transition.³⁷ Immediately after iodine was mixed with an excess ϵ -CL in CHCl_3 , a strong absorption appeared at 366 nm characteristic of the presence of triiodide anion as shown in Figure 1. The indication that

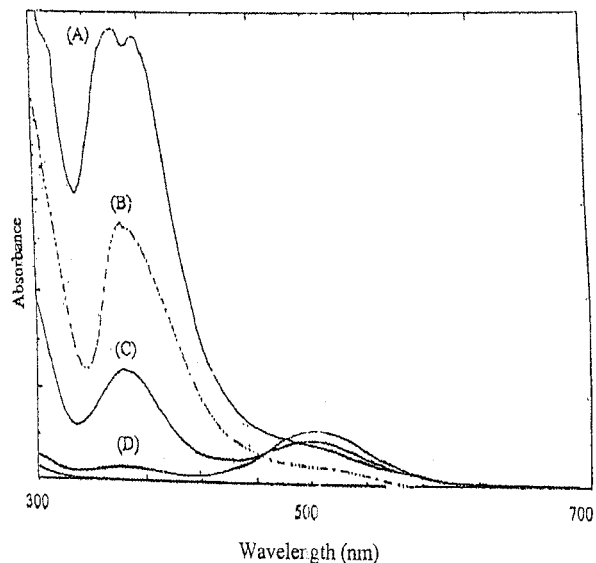


Figure 1. Electronic spectra: iodine in CHCl_3 (D) and $\epsilon\text{-CL}:\text{I}_2$ CT complexes in CHCl_3 (from bottom to top, at increasing iodine concentration).

$\epsilon\text{-CL}$ interacts with iodine chemically can be described as an $\epsilon\text{-CL}$ protonic form $(\epsilon\text{-CL})^+$, and a triiodide results from the development of a new charge-transfer band at 250 nm with a shoulder at 290 nm (spectrum not shown) that is comparable in shape and absorption wavelength to the charge-transfer band in iodine–ether complexes.^{38,39} No absorption appears at 450 nm, indicating the absence of the I_5^- species, even in the presence of an excess of iodine.^{40,41} The concentration of unreacted iodine (502 nm band) also stayed nearly constant throughout the polymerization. At the end of the reaction, however, the absorption of iodine increased considerably, and the reaction mixture became turbid. The unreacted iodine may be free or weakly interacting (π -complexed) with monomer.

Figure 2 depicts the curves generated for percent conversion versus time in iodine-promoted bulk polymerization of $\epsilon\text{-CL}$. The monomer conversion was determined by ^1H NMR spectroscopy. The polymerization reaction was carried out in a capillary using D_2O at 25 °C. To perform quantitative experiments, the following conditions were used: $nt = 1$ (only one acquisition to ensure that the measurement is the instantaneous one and not the average), and $d1 = 900$ (delay time between measures). The conversion was calculated from the integration ratio of CH_2^* methylene protons of PCL ($-\text{O}-\text{CH}_2^*-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CO}-\text{O}-$)_n and the same protons of the

cyclic monomer. In each system, up to 2 h, a monotonic increase was observed in monomer conversion, implying that consumption is not zero-order with respect to monomer concentration. As a general trend, higher levels of monomer conversion are achieved by decreasing the level of initiator (I_2) and increasing the $\epsilon\text{-CL}/\text{I}_2$ molar ratio. The strong concentration dependence of the reaction may appear to be consistent with a radical coupling step. However, the reaction mechanism is complicated by addition of iodine to the $\epsilon\text{-CL}$ rings, either by attack of an iodide species on cationic intermediates or through electrophilic addition.

^1H NMR and FTIR spectra of PCL obtained after 2.5 h reaction time were recorded and are shown in Figures 3 and 4. The observed assignments of chemical shifts for protons (^1H NMR) and the $\text{C}=\text{O}$ band (1720 cm^{-1}) of the poly($\epsilon\text{-CL}$) obtained by iodine-promoted polymerization agree with those reported in the literature.^{42,43}

The molecular weight distributions (MWDs) of PCL may provide valuable knowledge on the polymerization mechanism. Figure 5 illustrates the GPC curves for PCL obtained by bulk iodine polymerization at 25 and 70 °C. The reaction mixture became very viscous or almost solid; further

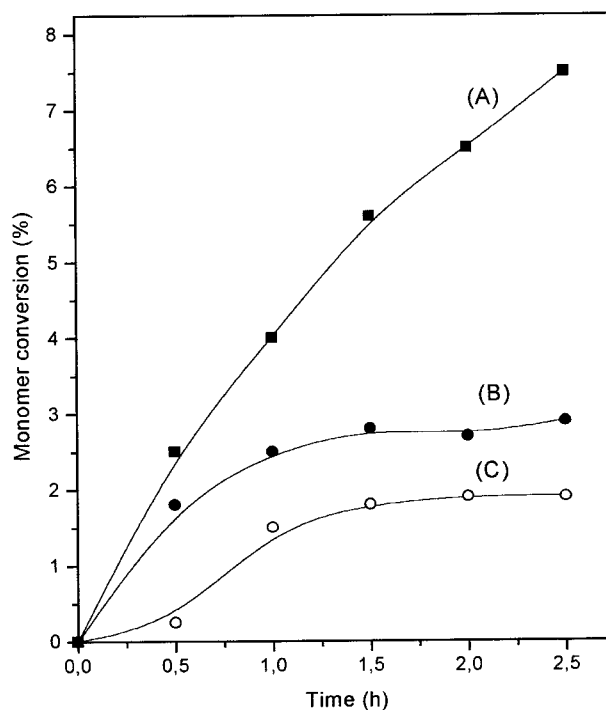


Figure 2. Monomer conversion at short reaction times. $[\epsilon\text{-CL}]/[\text{I}_2]$: 20:1 (A), 20:4 (B), and 20:10 (C).

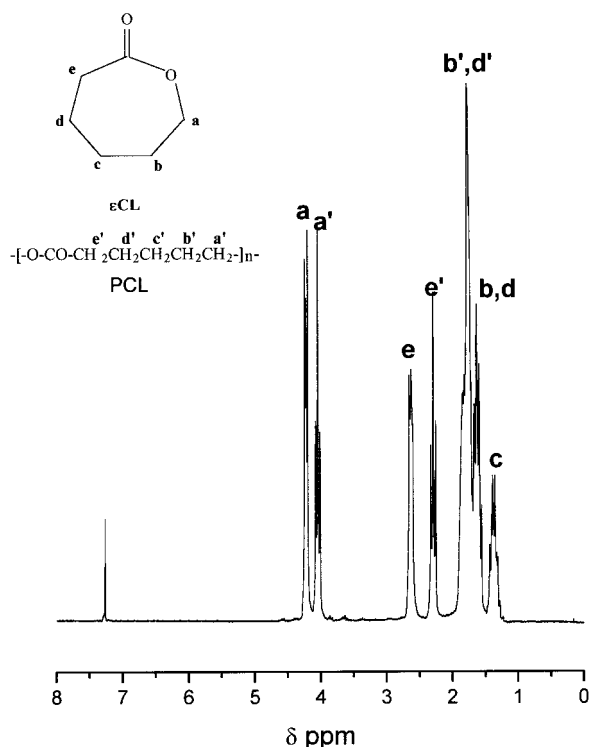


Figure 3. 400-MHz ^1H NMR spectra recorded in CDCl_3 of PCL at low percent conversion (2 h reaction time).

polymerization and depolymerization reactions still occurred slowly with increasing M_w , thus broadening the M_w/M_n . Because the M_n is considerably influenced by the low molecular weight fractions in the polymer and does not clearly reflect the molecular weight increase in a polycondensation-type reaction, M_w must be used to compare the molecular weight of the polymer. The M_w of the polymer obtained at 70 °C was higher than those obtained at 25 °C as a result of the mobility of the reactant species in the reaction mixture.

The MWD is very narrow at 25 °C, the polydispersity index (M_w/M_n) being equal to 1.3. The molecular weight obtained by iodine-promoted bulk polymerization alone at 70 °C under similar conditions increased only slightly at higher temperatures, and the MWD became rather broad ($M_w/M_n = 1.7$). The narrow MWD at higher temperatures is probably ascribed to the mobility of the reactant species in the reaction mixture. The MWD dependence on temperature may be indicative of the characteristic living (or at least long-lived) propagating species commonly observed in systems that made use of the iodine as a polymerization catalyst.⁴⁴

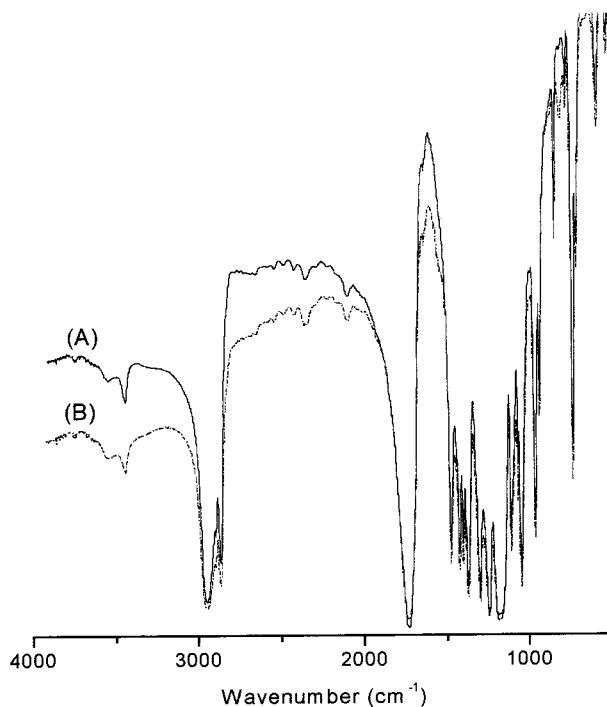


Figure 4. FTIR spectra of PCL obtained by bulk polymerization by iodine (A) and ZnCl_2 (B).

The application of *ab initio* and semiempirical calculations to radical processes in polymerization reactions has been extensively documented

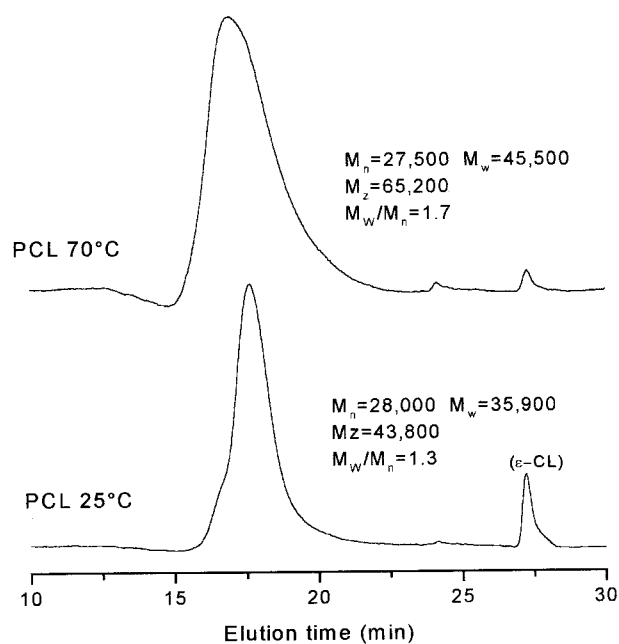
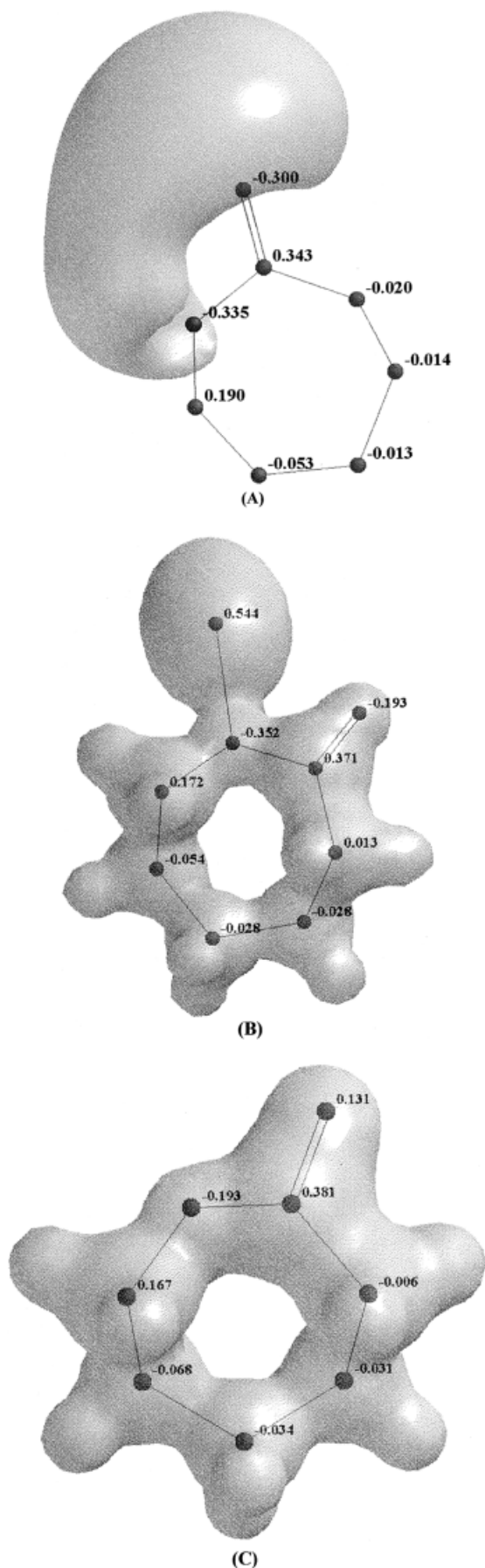


Figure 5. GPC profile of iodine-promoted polymerization of ϵ -caprolactone.



in the literature.^{45,46} In this work, MNDO-d calculations were used to study the strength of the bond between a propagating free-radical chain end and a free-radical species that reversibly reacts with it, the key to obtain reasonable reaction rates and narrow polydispersivity.

The use of the MNDO-d method that includes d-functions on iodine may be a rapid prototyping method to reliable reaction potential surfaces for the establishment of the structures models of the propagating species promoted by iodine.

The electrostatic potential, ϵ_p , defined as the energy of the interaction of a positive point charge with the nuclei and electrons may be used for obtaining the isosurfaces of organic molecules.

The isosurface of a molecule may be obtained from the electrostatic potential equation

$$\epsilon_p = \sum_A \frac{Z_A}{R_{Ap}} - \sum_{\mu\nu} P_{\mu\nu} \int \frac{\phi_{\mu}^*(r)\phi_{\nu}(r)}{r_{rp}} dr$$

where the first summation is over nuclei A, Z are atomic numbers, and R are distances between the nuclei and the point charge. The second summation is over basis functions, ϕ , P is the density matrix, and the integrals reflect Coulombic interactions between the electron and the point charge.

Despite its simplicity, the isosurfaces may be very useful in providing detailed information on the contributions of specific regions of the molecules to the chemical reactivity. An isosurface for which the electrostatic potential is negative (a negative isopotential surface) delineates regions in a molecule that are subject to electrophilic attack.

The electrostatic potential of the ϵ -CL monomer, CTC ϵ -CL:I₂, and the nucleophilic (ϵ -CL)⁺ species are displayed in Figure 6. In Figure 6(A), the highly negative isosurface value of the ϵ -CL monomer (-20 kcal/mol) indicates that the carbonyl and oxygen atoms are highly reactive sites with a strong electrophilic character.

The large size and polarizability of iodine leads to the halogen ability to form stable polycordi-

Figure 6. Isopotential surfaces generated by MNDO-d methods for: ϵ -CL (A), (ϵ -CL:I)⁺ CTC (B), and (ϵ -CL)⁺ CTC (C) with Mülliken charges [isovalues = -20.0 Kcal/mol (A), 264.19 kcal/mol (B), and 264.121 Kcal/mol (C)].

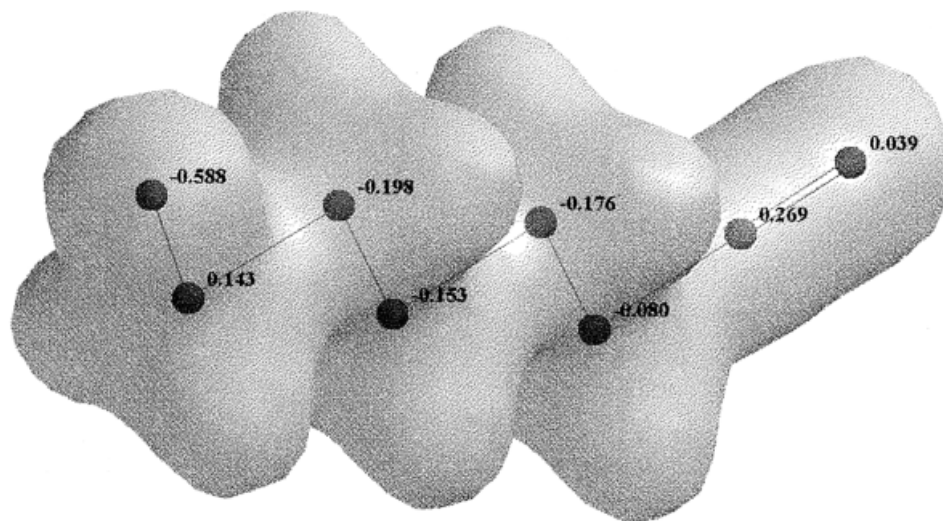


Figure 7. Isopotential surface and Mulliken charges for the $(\epsilon\text{-CL})^+$ chain (isovalues = 0.08 Kcal/mol).

nate, multivalent compounds (I_3^- , I_5^-) and a strong tendency to form CTCs even with weak donors.⁴⁷

Figure 6(B) illustrates the $\epsilon\text{-CL}$ isopotential surface after interaction of the monomer with iodine and formation of the positively charged $(\epsilon\text{-CL:I})^+$ CTC. The $(\epsilon\text{-CL:I})^+$ isopotential surfaces assume a positive value (262.92 kcal/mol) indicating the strong tendency to form CTCs with a nucleophilic character. Such $(\epsilon\text{-CL:I})^+$ complexes usually have a large contribution from dative structures resulting frequently in the formation of the triiodide (I_3^-) species.

If the charge-transfer interaction is obtained by the interaction between iodine and $\epsilon\text{-CL}$ with formation of the I_3^- species, the possible bonding sites are the carbonyl and oxygen lone pair. The interaction through the oxygen should be qualitatively similar to the protonation because of the strong electron-acceptor characteristic of iodine. These results agree with the UV-vis spectroscopy that indicate, as mentioned previously, the formation of I_3^- . The fact that the highly positive isovalue, 264.19 kcal/mol, obtained from the isopotential surfaces of protonated $\epsilon\text{-CL}$ ($\epsilon\text{-CL}^+$) [Fig. 6(C)] suggests that the positively charged $\epsilon\text{-CL}$ ring may be formed after the interaction of the iodine with $\epsilon\text{-CL}$.

The results agree with the Mulliken charges of the C=O and C—O bonds in $\epsilon\text{-CL}$ monomer, $(\epsilon\text{-CL:I})^+$, and the protonated $\epsilon\text{-CL}$ rings $(\epsilon\text{-CL})^+$ [Fig. 6(A–C)]. The greater negative charge of the C=O bonds in the $\epsilon\text{-CL}$ as compared with the CTC enables one to suggest that in the presence

of iodine the associate type of C—O and iodine is more probable than $\text{C}=\text{O} \cdots \text{I}_3^-$ associate even at room temperature.

Figure 7 shows the isopotential surface and Mulliken charges for the proposed $(\epsilon\text{-CL})^+$ opening-ring chain. The results suggest that the inter-

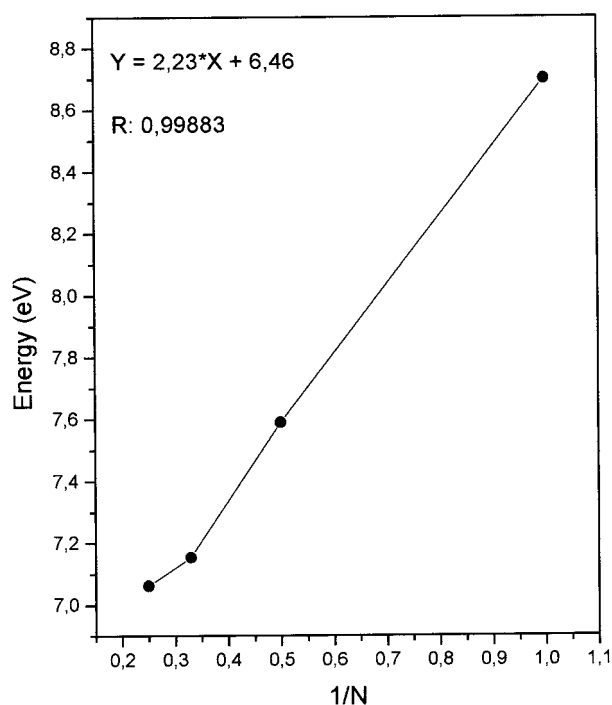


Figure 8. Band gaps (or HOMO/LUMO differences) of excitation energies versus inverse number of CL unites estimated with MNDO-d.

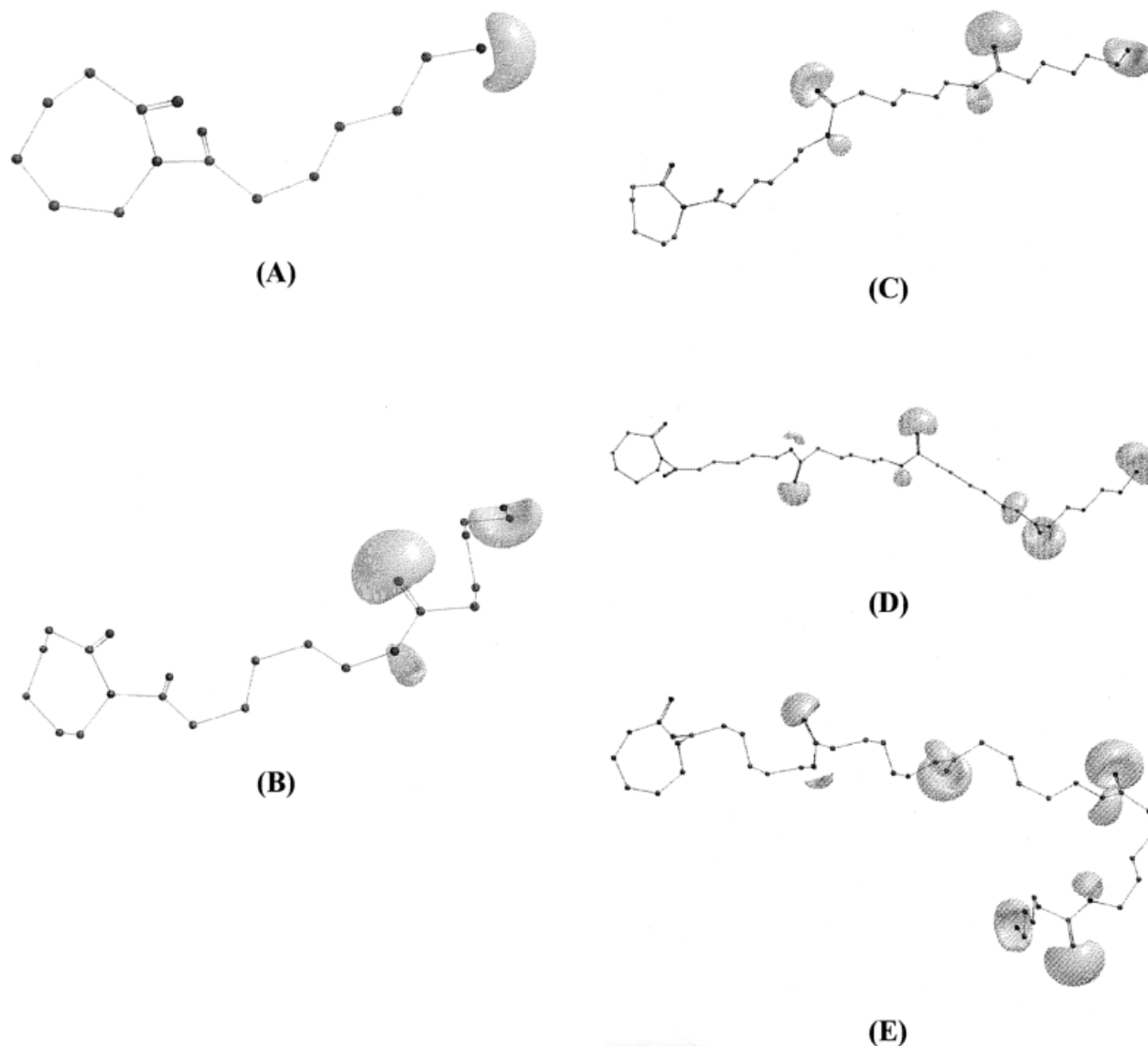


Figure 9. Structures of the aggregates: AB_1 (A), AB_2 (B), AB_3 (C), AB_4 (D), and AB_5 (E) predicted by MNDO-d calculations. A is the $(\epsilon\text{-CL})^+$ ring, and B is the $\epsilon\text{-CL}$ chain units (isovalues = -20 Kcal/mol).

action between $\epsilon\text{-CL}$ and triiodide reduce the charge density of both $\text{C}=\text{O}$ and $\text{C}-\text{O}$ bonds with the displacement to electronic charge ring to the iodine-promoting the ring opening of the monomer and formation of the highly polarized polymerization precursor $(\epsilon\text{-CL})^+$ structure. Thus, in this bulk polymerization promoted by iodine, a highly nucleophilic ester may be formed by protonation of the chain-starting reaction [Fig. 6(A)]. The growth of the polymer chains can ensue from both intermediates by an electrophilic attack of either a monomer or a polymer chain. However, the possibility that the proposed opening chain

attacks the formed CTC has also been considered. The bonding of $\text{C}-\text{O}$ should be weakened by the complexation, and the propagating species may attack the complex much easier than the $\epsilon\text{-CL}$, therefore facilitating the polymerization.

The energetic properties used to analyze the proposed $(\epsilon\text{-CL})^+$ iodine-promoted bulk polymerization model may be the energy gap, calculated as the energy difference between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO).

The importance of frontier orbitals and their current considerable interest lie in the roles they

play in molecular properties, particularly the reactions that molecules can undergo.⁴⁸ Their importance stems in part from their role in governing the energy needed to rearrange the electrons in a molecule, and the LUMO–HOMO gap is the minimum electronic excitation energy. The HOMO/LUMO difference at the MNDO level does not closely relate to excitation energies because of the absence of orbital relaxation effects.⁴⁹

Figure 8 shows the band gaps for infinite chains of PCL determined by plotting the excitation energies calculated at the MNDO level (HOMO/LUMO differences) from PCL oligomers against the inverse of the number of ϵ -CL units ($n = 1$ –5) and extrapolating the number of units to infinity. The band gaps of PCL oligomers larger than dimers increase with increasing length that may be due to the onset of a helical structure.⁵⁰ Band gaps from MNDO (HOMO–LUMO differences) either agree with the experimental UV–vis spectrum obtained in this work.

Figure 9 indicates that the lowest energy conformation of the PCL oligomers at the MNDO level are all zigzag structures through the pentamer possibly because of the planarity degree of the lactone units in the polymeric chain or other environmental effects such as solvating or inter-chain interactions.

From an inspection of the molecular orbitals of two ϵ -CL interacting fragments in Figure 9, there are terminal electrophilic sites concentrated to the C=O and C–O bonds maintaining a weakly lone pair character. The lone pair in the oligomeric PCL structure may be important to the controlled synthesis of the polyester.

CONCLUSION

In conclusion we have shown that the ring-opening polymerization of ϵ -CL can be promoted by iodine to render poly(ϵ -CL). The reaction is simple and carried out under mild conditions (lower temperature) as compared with conventional thermal methods for ring opening of ϵ -CL polymerization. The reaction mechanism appears to involve the initial formation of a protonated ϵ -CL that ring opens, followed by subsequent polymerization by radical coupling. However, speculation about a possible mechanism of the polymerization by iodine is complicated by addition of iodide species on cationic intermediates, or through electrophilic addition. Further investigations into the

nature and scope of this ring-opening polymerization will be needed to assess its potential.

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