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Physical Properties of Aliphatic Polycarbonates Made from CO₂ and Epoxides

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ABSTRACT: A homologous series of aliphatic polycarbonates with different side-chain lengths was synthesized by ring-opening polymerization of terminal epoxides with CO₂ using zinc adipionate as catalyst [patented process of Empower Materials (formerly PAC Polymers Inc.)]. Additionally, a polycarbonate was made having a cyclohexane unit in its backbone, together with a terpolymer having both cyclohexane and propylene units. After characterization of thermal properties the aliphatic polycarbonates were found to be completely amorphous. Polycarbonates derived from long-chain epoxides showed a glass-transition temperature (T_g) below room temperature, whereas polycarbonates derived from cyclohexene oxide showed a T_g of 105°C, the highest yet reported for this class of polymers. The initial decomposition temperature of the polymers in air and nitrogen atmospheres was found to be less than 300°C. The mechanical properties and the dynamic mechanical relaxation behavior of the polymers were also reported. The effect of the chemical structure on the physical properties of aliphatic polycarbonates was discussed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1163–1176, 2003

Key words: aliphatic polycarbonates; physical properties; glass-transition temperature; thermal degradation; epoxides

INTRODUCTION

Aromatic polycarbonates are well-known engineering thermoplastics with diverse end applications. Aliphatic polycarbonates are relatively new thermoplastics first synthesized by Inoue[1,2] in 1969. They have found uses in a number of applications such as cost-effective additives for improving printability and processibility of polyolefins, and reducing shrinkage in calendered polypropylene.[3–5] They are used to improve the mechanical properties of styrene butadiene rubber[6] and for forming interpenetrating networks (IPNs) with other polymers.[7] They also show potential as biodegradable and biocompatible materials. The possibilities of their use in tissue implants,[8] as matrices for drug delivery systems, as packaging films, and in medical sutures[9] are being investigated.

The reports of the physical properties of aliphatic polycarbonates covering a wide range of polymers are few.[3] The aim of this work was to determine primarily the physical properties of a homologous series of aliphatic 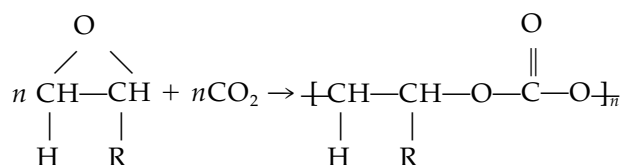polycarbonates. The reported data consists of thermal and mechanical properties and observations regarding the relationships between the molecular structure and these properties.

EXPERIMENTAL

Materials

The materials used were synthesized by Dr. Semenov through ring-opening polymerization of terminal epoxides with CO₂, using the patented method of PAC Polymers Inc. (U.S. Patent 4,665,136). The method uses zinc adipionate as catalyst under standard conditions of 25–35 atm pressure and a temperature of 45–55°C. The polymers were synthesized using corresponding alkyl epoxides and CO₂ in standard conditions. The process is the property of Empower Materials and more details cannot be given here.

The reaction for the synthesis of these aliphatic polycarbonates is given by the following general reaction scheme:

$$n\ \overset{\displaystyle O}{\overset{\diagup\ \ \diagdown}{CH{-}CH}} + nCO_2 \rightarrow \underset{\underset{H}{|}\ \ \underset{R}{|}}{\left[CH{-}CH{-}O{-}\overset{\overset{O}{\|}}{C}{-}O\right]_n}$$

All of the polymers studied were found to be completely amorphous, unlike some reports in the litera-
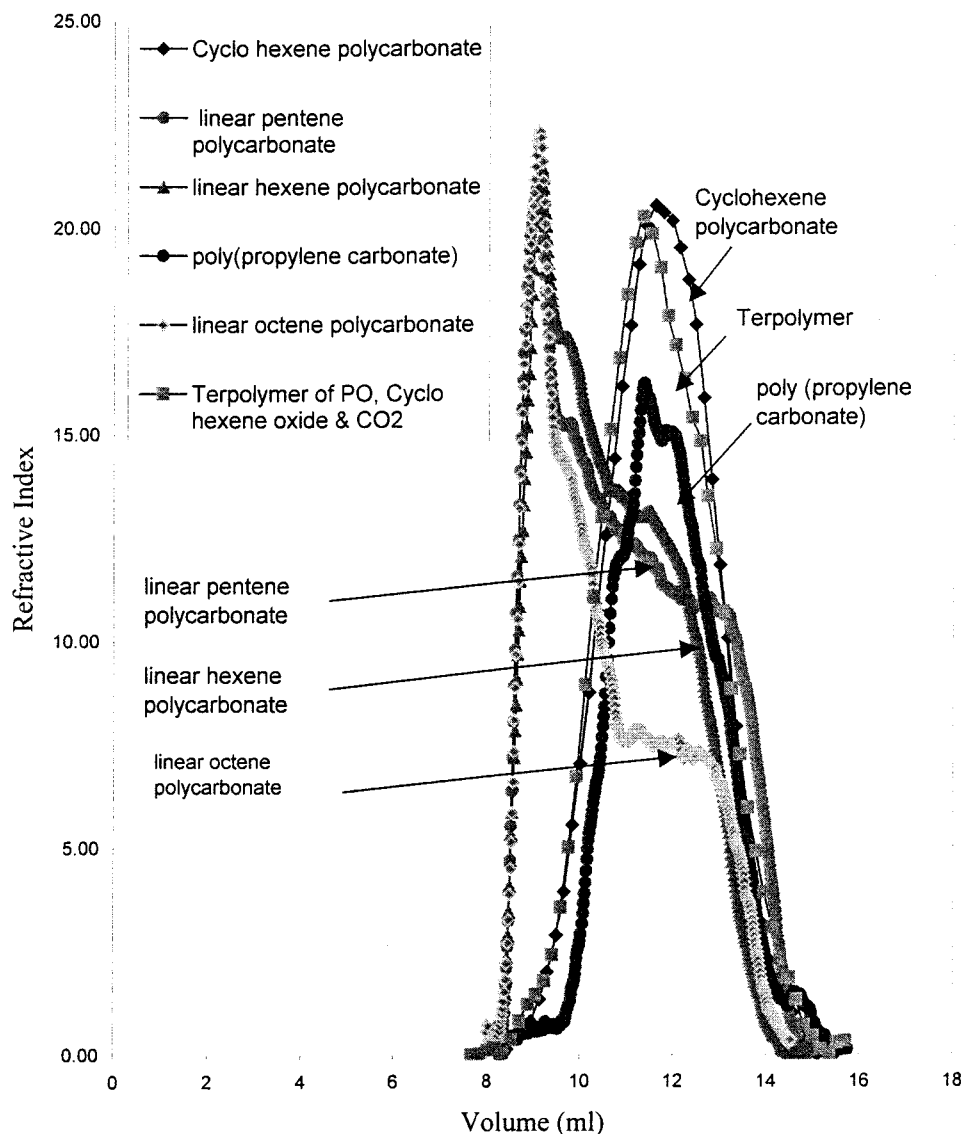
Figure 1 GPC curves for the polymers in THF solution.

ture. This is undoubtedly attributed to the incorporation of polyether groups into the main chain of the polymer through a side reaction. Although ether groups could be detected in FTIR studies, the amounts present were not quantified at this stage. Simply they

TABLE I
Weight-Average and Number-Average Molecular Weights and Polydispersity Indices for Aliphatic Polycarbonates Expressed as Polystyrene Equivalents

Polymer	M_w	M_n	PDI
Polypropylene carbonate	28,900	7,540	3.83
Poly(linear pentene carbonate)	44,400	7,500	5.13
Poly(linear hexene carbonate)	−45,500	9,490	4.79
Poly(linear octene carbonate)	49,400	10,500	4.70
Poly(cyclohexene carbonate)	33,800	7,980	4.23
Terpolymer of CO_2, propylene oxide (20%), and cyclohexene oxide (80%)	35,200	8,680	5.27

were enough to prevent crystallization and hence would be the order of 3–5% if randomly incorporated into the chain.

The polymers produced from the corresponding terminal epoxides were poly(ethylene carbonate) (**1**), poly(propylene carbonate) (**2**), linear pentene polycarbonate (**3**), linear hexene polycarbonate (**4**), linear octene polycarbonate (**5**), cyclohexene polycarbonate (**6**), and the terpolymer (**7**) made from 80% cyclohexene oxide and 20% propylene oxide. The sample code includes the monomer type with the number of carbon atoms followed by the term PC.

Further, there are at least two confusing nomenclature systems in use; for example, poly(ethylene carbonate) may be referred to as ethylene polycarbonate by analogy with the system used for the aromatic polycarbonates. It should also be noted that the same nomenclature systems are used to designate the poly-
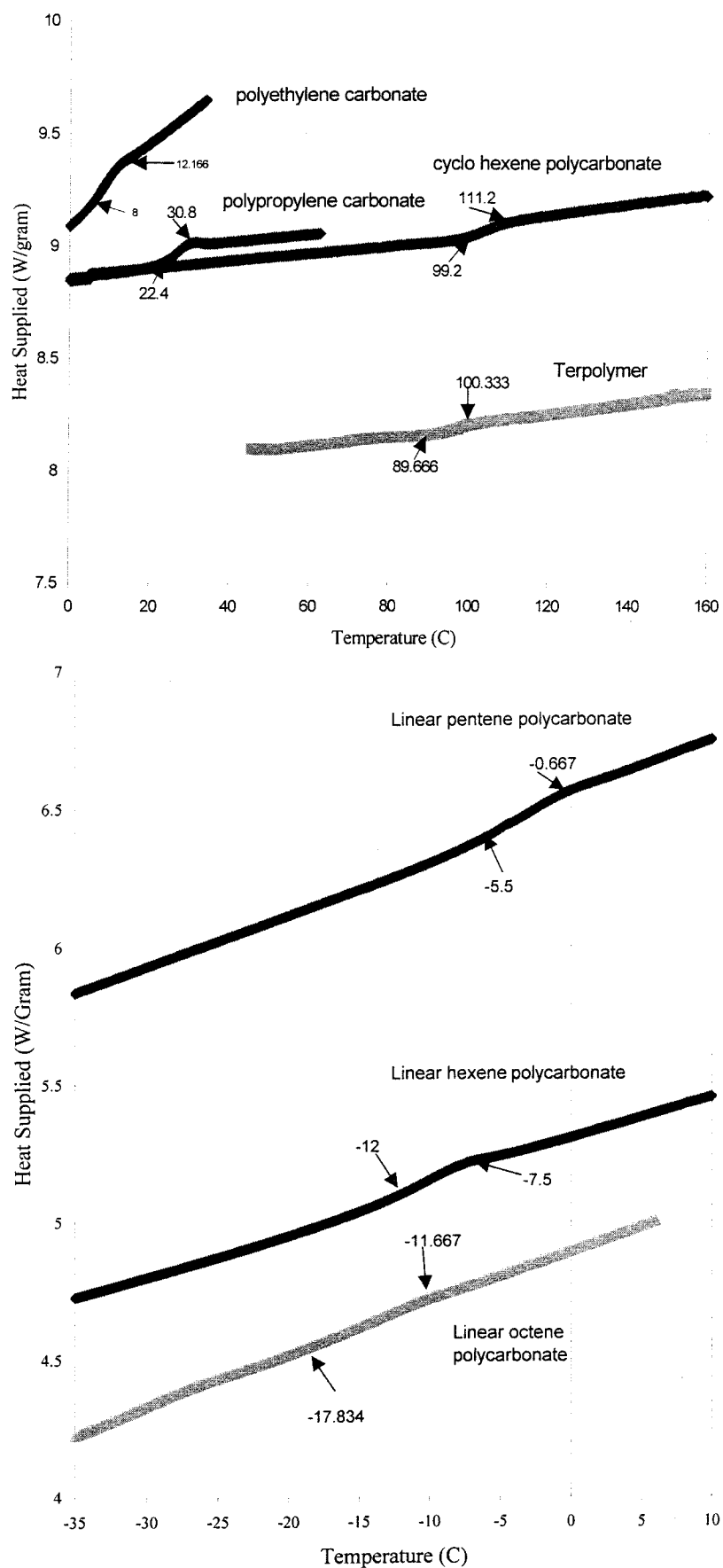
Figure 2 DSC curves showing the glass transitions of the series of aliphatic polycarbonates.

TABLE II
Glass Transition Temperature T_g Range and Inflection Point for Aliphatic Polycarbonates

Polymer	DMA (Hz)			DSC T_g (°C)	
	1.1	11	110	Range	Inflection point
Polyethylene carbonate	19.1	25.7	30.8	8 to 12	10
Polypropylene carbonate	43.4	50.4	57.2	22 to 30	28
Poly(linear pentene carbonate)	12.4	18.1	26.3	−6 to −1	−4
Poly(linear hexene carbonate)	5.6	11.4	17.2	−12 to −7	−10
Poly(linear octene carbonate)	1.2	6.0	9.1	−18 to −12	−16
Poly(cyclohexene carbonate)	136.6	143.7	154.7	99 to 111	105
Terpolymer of CO_2, propylene oxide (20%), and cyclohexene oxide (80%)	119.6	126.2	137.6	93 to 100	97

mers synthesized from different routes and raw materials. In fact it can be verified that the chemical structure of the polymer manufactured from 1,8-octene glycol and dimethyl carbonate will give semi-crystalline[10] linear octene polycarbonate with all methylene groups in the main chain, whereas 1,2-octene oxide and CO_2 will yield amorphous linear octene polycarbonate (**5**) with $-(CH_2)_5-CH_3$ as a side chain. Hence the route of synthesis of aliphatic poly-

carbonates should be taken into account before comparing their properties.

Molecular weight characterization

Gel permeation chromatography (GPC) was performed using a Waters 590 model (Waters Chromatography Division/Millipore, Milford, MA) with μ-Styragel columns and THF as the solvent. Solutions
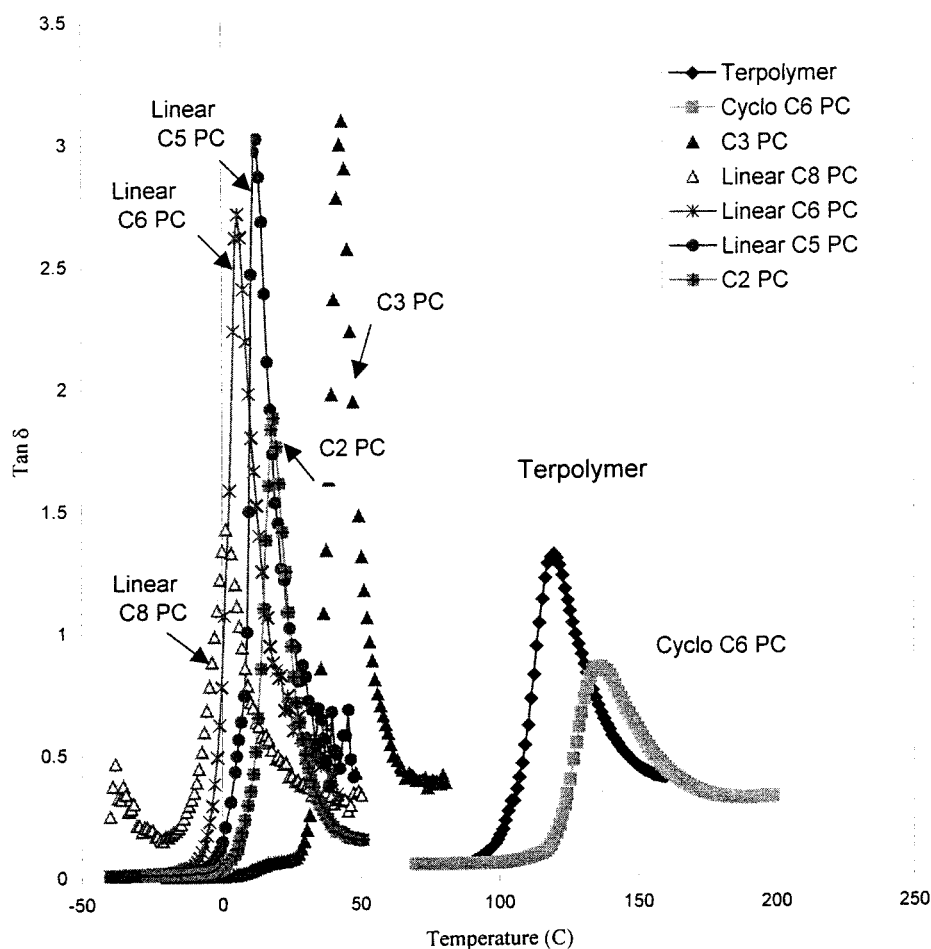

Figure 3 Tan δ for the series of aliphatic polycarbonates at 1.1 Hz using DMA.

TABLE III
Activation Energies and Activation Entropies of the Glass-Transition Processes of Aliphatic Polycarbonates Obtained from DMA

Polymer	Activation energy (kJ/mol)	Activation entropy at 1.1 Hz ($J/mol^{-1}/K^{-1}$)
Polyethylene carbonate	288.6	751
Polypropylene carbonate	290.0	679
Poly(linear pentene carbonate)	233.6	581
Poly(linear hexene carbonate)	267.1	722
Poly(linear octene carbonate)	368.9	1108
Poly(cyclohexene carbonate)	366.2	654
Terpolymer of CO_2, propylene oxide (20%), and cyclohexene oxide (80%)	336.4	617

of concentration approximately 9 mg/5 mL were used. The 200-μL solution was injected in the column with an operative flow rate of 1 mL/min at 40°C. The column was calibrated using polystyrene standards of molecular weights (in K) 240, 169, 95, 50, 17.5, and 3.5 under identical conditions. The column measures the differential refractive index of the solvent. Ethylene polycarbonate was not soluble in THF and could not be characterized.

The GPC curves of linear pentylene, hexane, and octene polycarbonates did not show a normal distribution, although the solutions were stable without precipitation after 7 days (see Fig. 1). These three polymers showed a significant population of higher
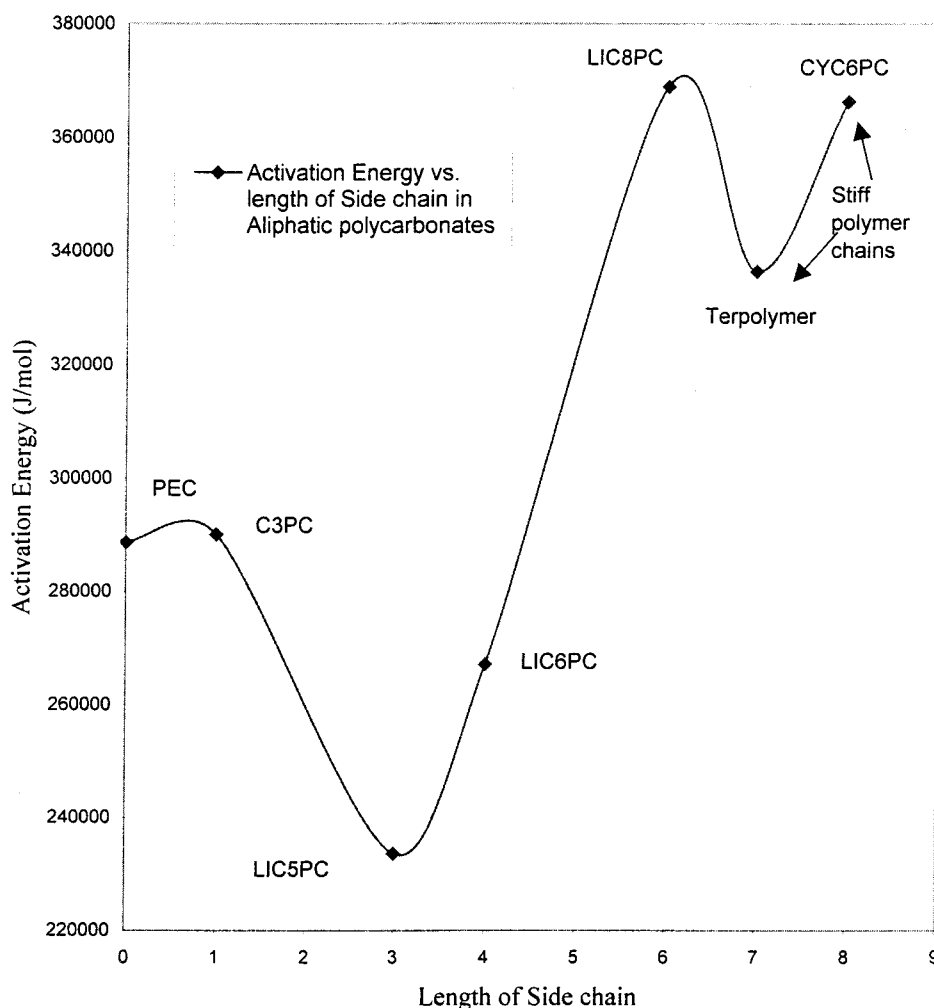

Figure 4 Activation energy of the glass transition versus length of side chain in aliphatic polycarbonates.
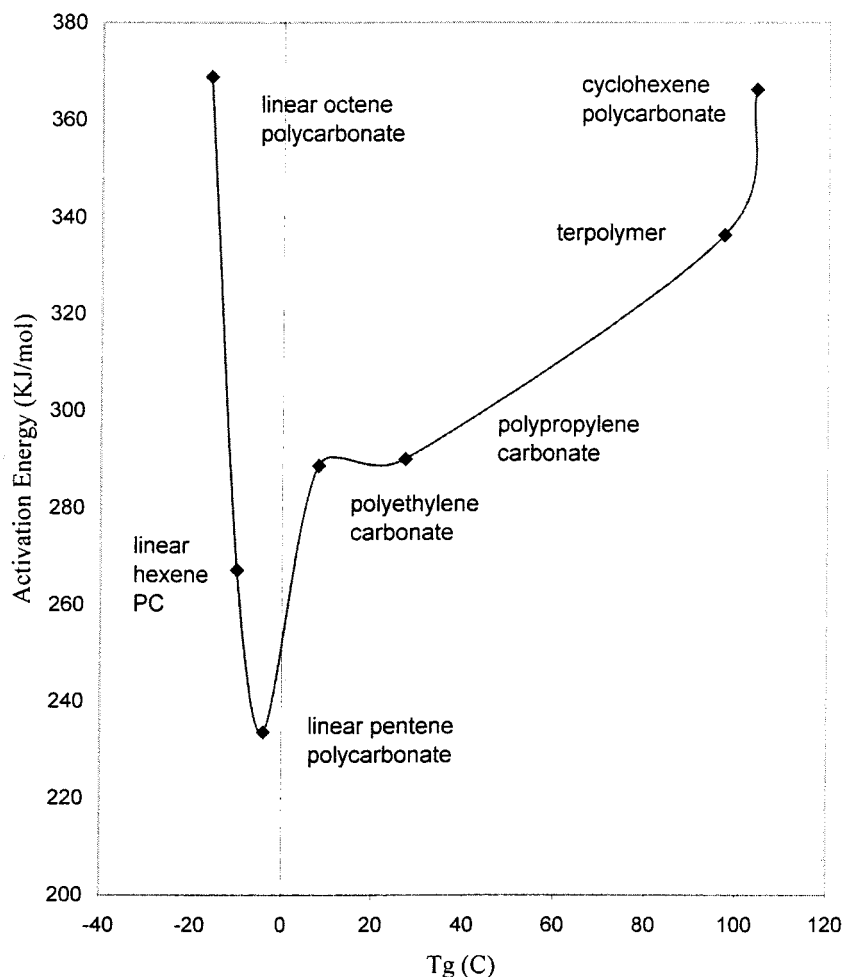
Figure 5 Activation energy of the glass transition versus glass-transition temperature of aliphatic polycarbonates.

molecular weight molecules. However, there was also a significant population of low molecular weight molecules and the distribution was bimodal and broad. The remaining polymers showed normal narrow distributions.

Absolute values of the molecular weights could not be calculated and so results are given in terms of polystyrene equivalents (see Table I).

Physical analytical methods

Differential scanning calorimetry (DSC) measurements were performed using a Perkin–Elmer DSC-7 instrument (Perkin Elmer Cetus Instruments, Norwalk, CT) at a heating rate of 10°C/min in a nitrogen atmosphere. The samples were in the form of thin films weighing 8–12 mg.

Dynamic mechanical analysis (DMA) was conducted using a Hewlett–Packard Rheovibron viscoelastometer AVD985 (Hewlett–Packard, Palo Alto, CA) according to the ASTM standard 5025. The instrument was designed to impose a sinusoidal strain, in tension, and measure the sinusoidal stress response of

the material with respect to amplitude and phase. The measurements were made at three frequencies, 1.1, 11, and 110 Hz, from temperatures of −150°C to the maximum possible above the glass-transition temperature of the sample, determined by mechanical stability.

Thermogravimetric analysis (TGA) was conducted with a Mettler thermogravimeter (TG50; Mettler Instruments, Greifensee, Switzerland) at a heating rate of 10°C/min in air and under a nitrogen atmosphere. Isothermal studies were conducted by heating the sample to a chosen temperature and holding it at that temperature for a chosen time in the thermogravimeter.

Tensile testing was carried out at room temperature using an Instron 1122 tensile tester and ASTM standard 882.

RESULTS AND DISCUSSION

The aliphatic polycarbonates synthesized using this method were found to be completely amorphous with no crystalline melting observed in the DSC scans. Crystalline growth could not be observed through an
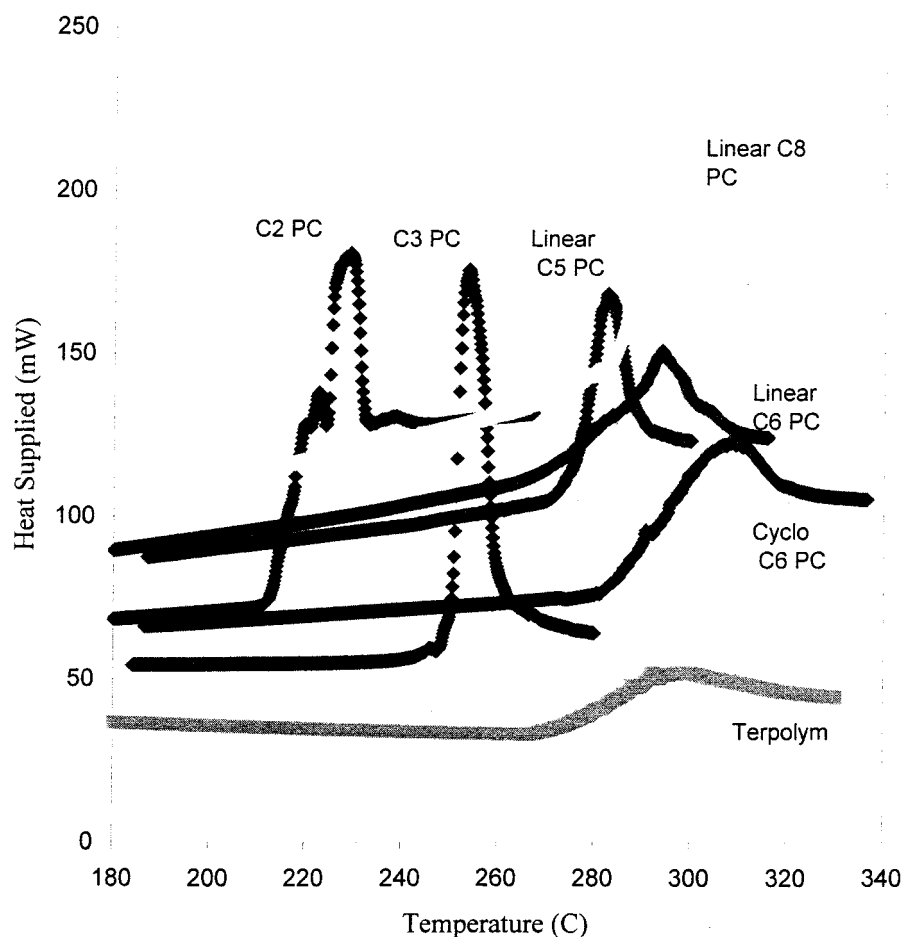
Figure 6 DSC curves showing the thermal degradation of aliphatic polycarbonates.

optical microscope after cooling the polymer melts. It therefore appears that the catalyst system used generates microstructural defects, which inhibit crystallization. In fact a distinct peak around 1200–1250 cm^{-1} was obtained in the FTIR scans for all polymers. This can be assigned to the ether group formed during the polymerization, indicating the presence of self-condensation of the epoxides as part of the polymerization process. This is not unlike the formation of diethylene glycol links in the synthesis of poly(ethylene terephthalate), a well-known phenomenon that has similar consequences in the properties developed.

The glass-transition temperature (T_g) of aliphatic polycarbonates was obtained from DSC scans, as shown in Figure 2. The glass transitions, not being first-order transitions, do not appear as peaks, but appear as changes of slope. The vertical axis represents heat capacity and a glass transition appears as a change in heat capacity, but usually spread over a range of temperature. The transition temperature is usually identified with the point of inflection. In some cases the range over which the transition occurs is quoted as well as the point of inflection, given that the range can be affected by the crystallinity, microstruc-

tural defect content, and comonomer content. The points of inflection and the temperature range over which each glass transition occurs in these aliphatic polycarbonates are presented in Table II.

The glass transition was also obtained from DMA scans, such as those studied at a frequency of 1.1 Hz, shown in Figure 3. The T_g in the case of DMA is

TABLE IV
DSC Degradation Temperatures and IDT for Aliphatic Polycarbonates

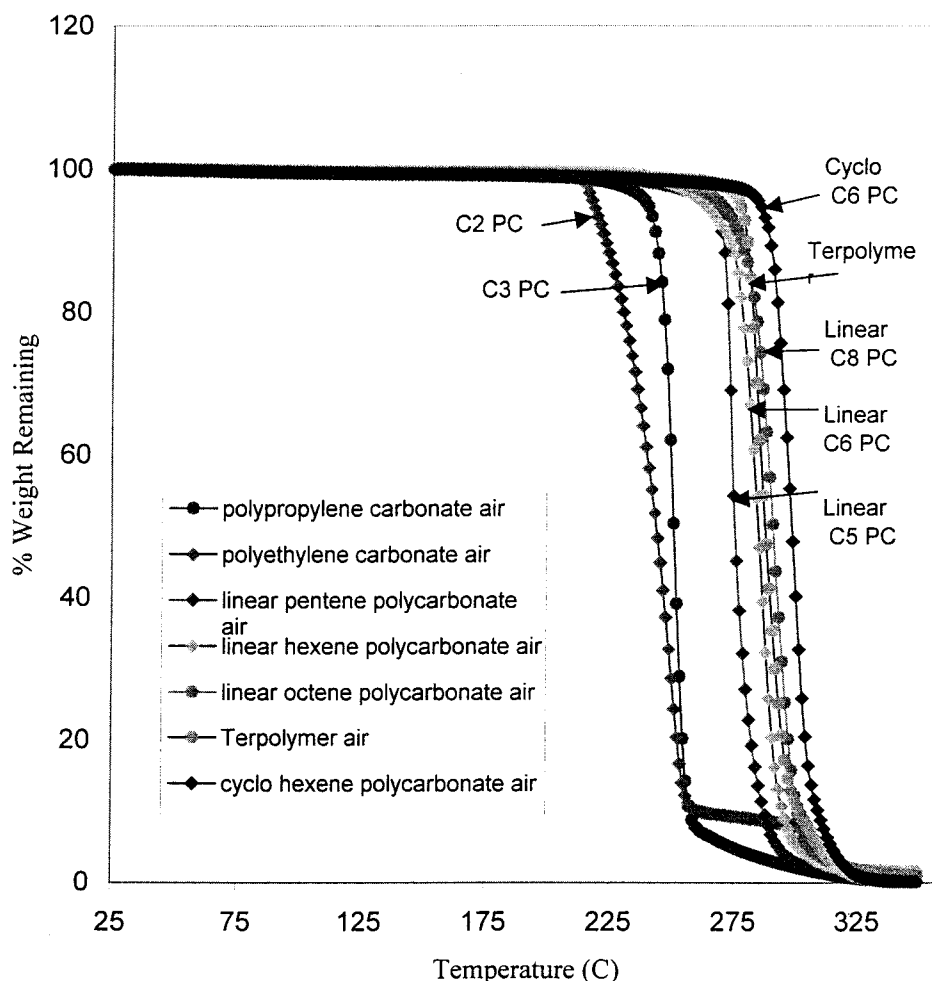| Polymer	DSC peak temperature (°C)	IDT (°C)	
		Air	Nitrogen
Polyethylene carbonate	229	217	232
Polypropylene carbonate	253	235	238
Poly(linear pentene carbonate)	283	246	270
Poly(linear hexene carbonate)	290	250	280
Poly(linear octene carbonate)	295	257	268
Poly(cyclohexene carbonate)	308	282	290
Terpolymer of CO$_2$, propylene oxide (20%), and cyclohexene oxide (80%)	296	265	276

Figure 7   TGA curves for aliphatic polycarbonates in air.

obtained as the peak of plots of loss tangent (tan δ) against the temperature. Values obtained from all three frequencies are presented in Table II for comparison with the DSC data.

The glass transition

From these figures it is seen that the glass-transition temperature decreases as the length of the side chain in the repeat unit increases, starting from polyethylene carbonate (**1**), with the one exception of the polypropylene carbonate (**2**). Because the polymers are polar chains with some dipolar interactions contributing to the bonding, it appears that the longer flexible side chains are pushing the main chains apart and lowering the glass transition through that mechanism. It is also possible that the amount of dipolar bonding per unit volume is being reduced as the hydrocarbon content of the polymers increases relative to the dipolar content. Hence the glass transition decreases from +10°C for polyethylene carbonate to −17°C for linear octene polycarbonate. In a manner similar to that established for polyacrylates, increasing the length of

the linear side chain does not increase the glass transition, but decreases it.[11] The process observed appears to be a case of internal plasticization.

These curves also show that the glass-transition temperature increases with increasing chain stiffness. Hence cyclohexene polycarbonate and the terpolymer, with the stiff cyclohexene ring as a part of main chain, have higher T_g values than those of other samples (i.e., 105 and 97°C, respectively). The –CH$_3$ side group in polypropylene carbonate makes the chain stiffer than that in polyethylene carbonate, which has only the H atom as a side group, thereby increasing the T_g from +10 to +28°C. The glass-transition temperatures obtained from DMA are greater than those obtained in DSC, increasing with the frequency of deformation, as is well known in other polymers. At all the frequencies studied, the T_g of the terpolymer is between that of cyclohexene polycarbonate and polypropylene carbonate and is found to be close to that predicted by the rule of mixtures.

Dynamic mechanical analysis was used to study the frequency dependence of the glass-transition temperature. It was observed that the T_g of the polymer
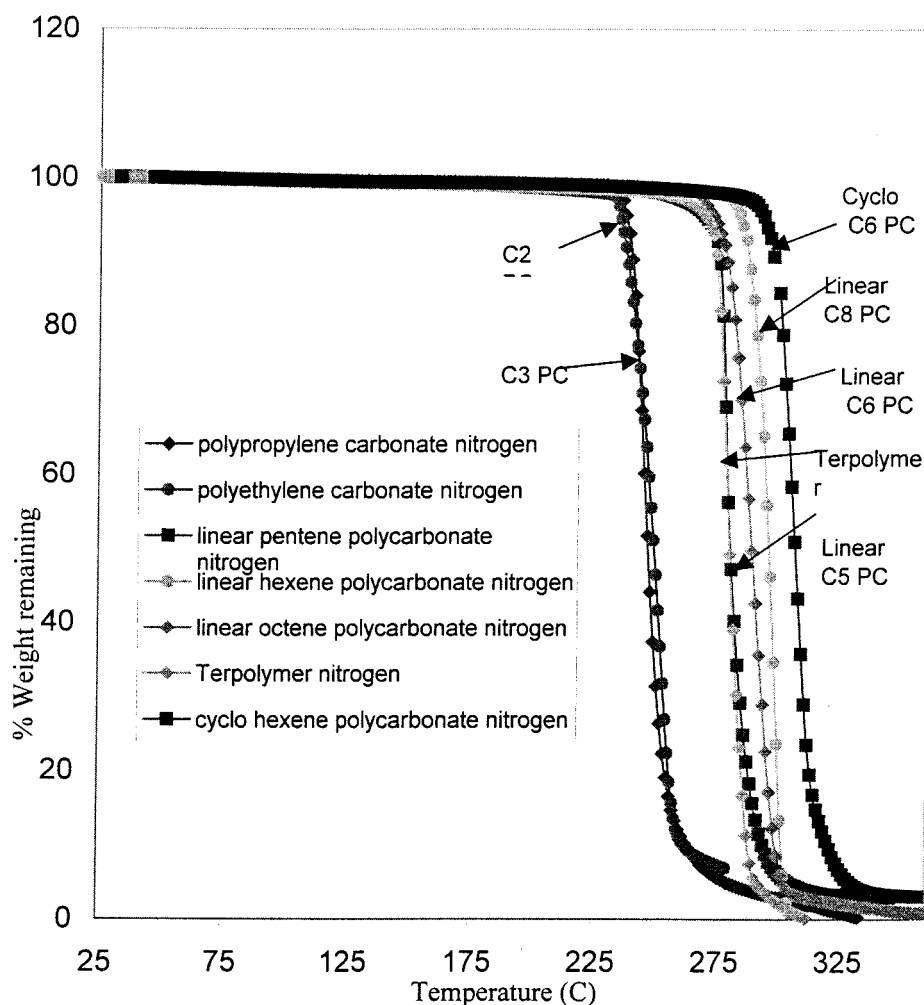
Figure 8 TGA curves for thermal degradation of aliphatic polycarbonates in nitrogen.

increases with the increase in frequency, as expected. The dependence of T_g on frequency gives the activation energy of the glass transition for the polymer as a first approximation, using the Arrhenius equation, because of the restricted frequency range possible in dynamic mechanical instrumentation:

$$\log(f) = A + \left(\frac{-\Delta E}{2.303RT_g}\right) \qquad (1)$$

where f is the frequency of the applied signal, ΔE is the activation energy of the relaxation process, R is the universal gas constant, and T_g is the glass-transition temperature.

The entropy of the polymeric relaxation process at each frequency can be obtained using the following formula:

$$\Delta E = RT_g\left[1 + \ln\left(\frac{k}{2\pi h}\right) + \ln\left(\frac{T_g}{f}\right)\right] + T_g\Delta S \qquad (2)$$

where k is Boltzmann's constant, h is Planck's constant, and ΔS is the activation entropy of the relaxation process.

Values of ΔE and ΔS for the aliphatic polycarbonates are presented in Table III. ΔE for aliphatic polycarbonates is plotted against the length of the side chain in Figure 4 and against the T_g in Figure 5.

It can be seen that the activation energy initially increases from (1) to (2) because of introduction of the $-CH_3$ group. It then decreases with increasing length of the flexible side chain [i.e., from (2) to (3)], which means that the flexible side chain has made the long-range conformational changes easier in the main chain. However, when the length of the side chain increases in the series from (3) to (5), the energy of activation increases. The increasingly longer side chains are capable of internal conformational change, which appears to lead to the side chain turning back on itself as the side chain length increases, making the conformational changes in the main chain more difficult. However, because the longer side chains progres-
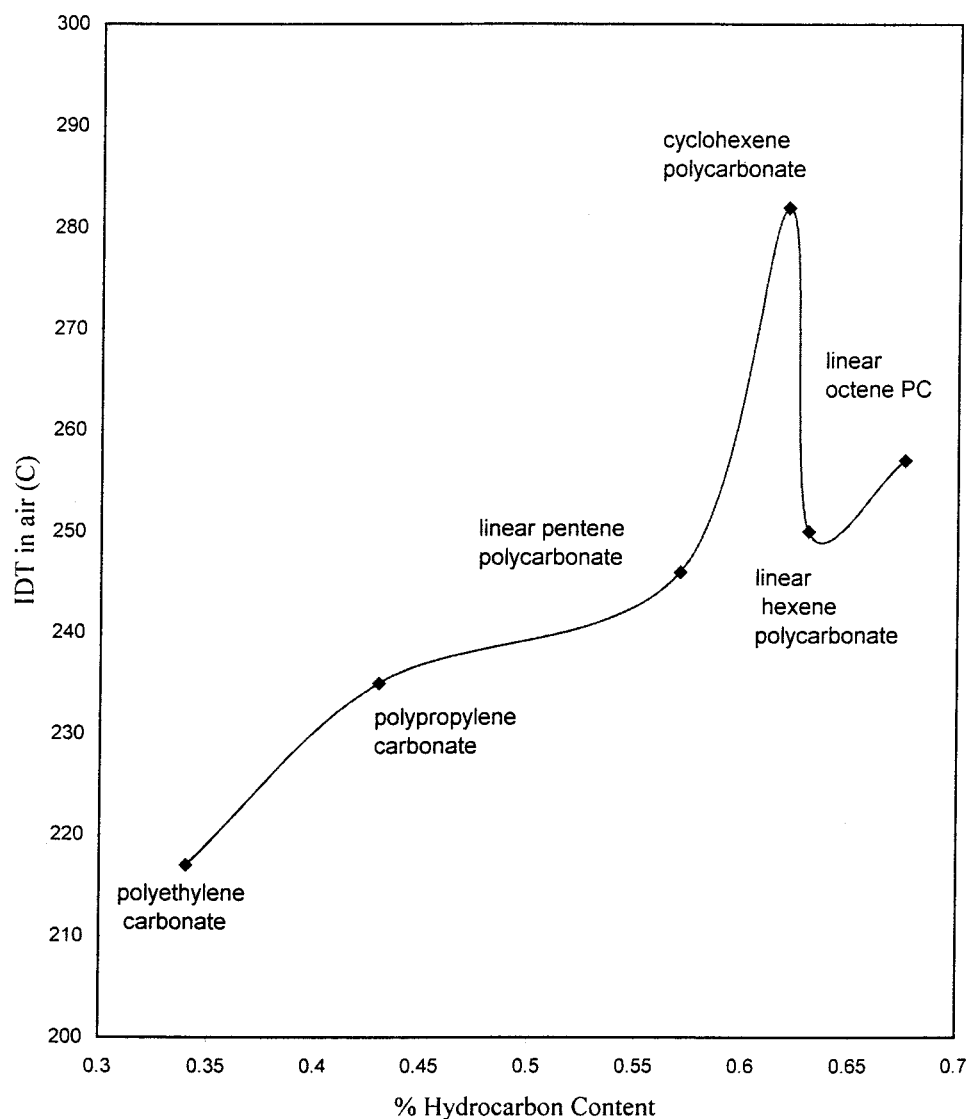
Figure 9 IDT in air plotted against the hydrocarbon content in aliphatic polycarbonates.

sively push the dipolar polymer chains apart, the T_g in fact decreases, even though the energy of activation increases. Hence linear octene polycarbonate has a higher activation energy than that of the other polycarbonates. The terpolymer (**7**) and cyclohexene polycarbonate have higher activation energies because of the presence of the stiff cyclohexane ring in the main chain. The ΔS (see Table III) follows the same trend as ΔE, given that the error in measurement of ΔE causes the error in the determination of ΔS and the errors arising from temperature and frequency reliability are negligibly small.

Thermal degradation

Thermal degradation of aliphatic polycarbonates was studied using DSC and TGA. In DSC the nitrogen atmosphere was maintained, whereas the TGA data

was obtained in air. The combined DSC scans for the degradation studies are as shown in Figure 6 and the data tabulated in Table IV. The TGA curves for the samples under air atmosphere are given in Figure 7. It can be seen that the aliphatic polycarbonates undergo thermal degradation at considerably lower temperatures than those of chain-reaction polymers such as polyethylene and polypropylene. It can also be seen that the thermal degradation occurs at higher temperatures in the nitrogen atmosphere (DSC) than in air (TGA) (see Fig. 8). Although the thermal degradation of the polymers cannot be eliminated completely during the industrial processing of polymers, it must be held to a minimum to keep the quality of the final products high. The degradation studies enable the estimation of the optimum operating conditions for the processing of these polymers. It is observed that the initial decomposition temperature (IDT) of ali-
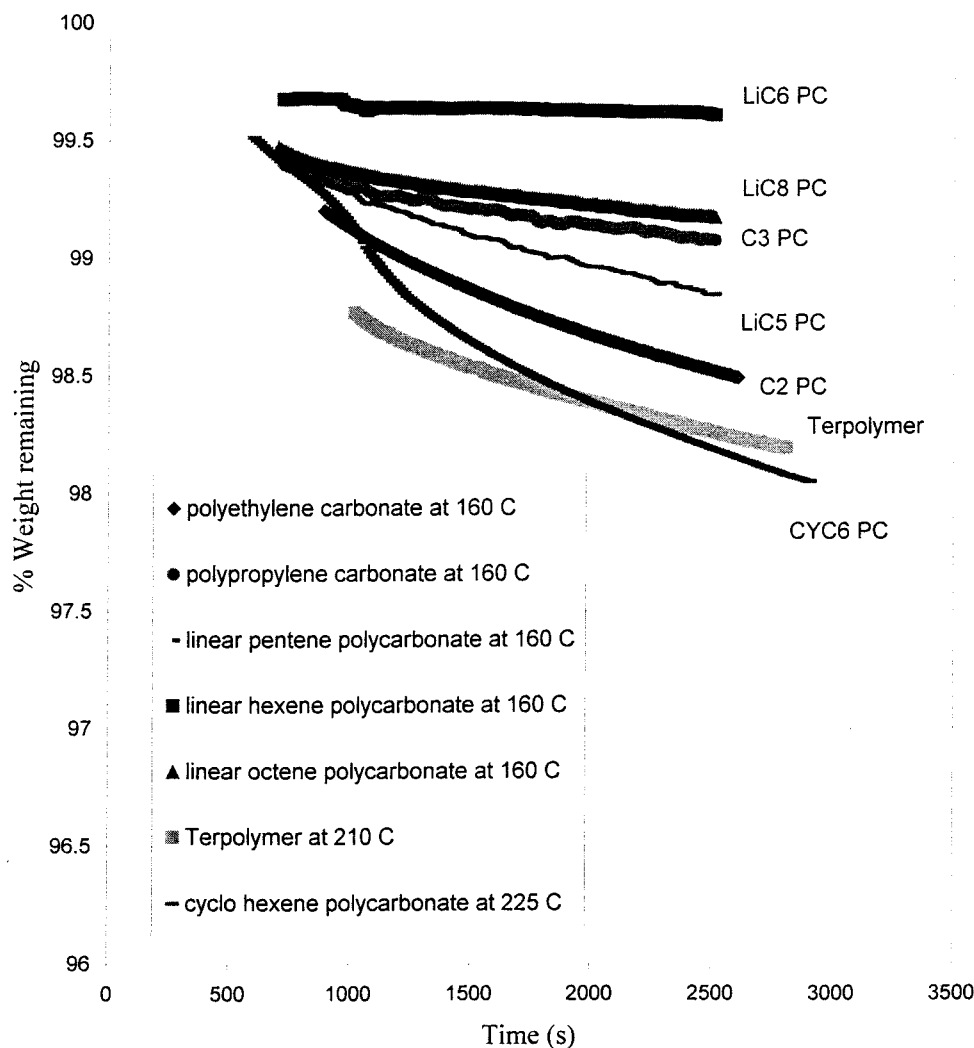
Figure 10 Isothermal TGA curves for aliphatic polycarbonates.

phatic polycarbonates increases with the increase in the hydrocarbon content in the polymer.

Thus the chemical structure affects not only the glass-transition temperature but also the degradation temperature and hence controls the processing temperature window for the given polymer. The plot of IDT (air) against the hydrocarbon content of the repeat unit of the polymer is shown in Figure 9. It shows that cyclohexene polycarbonate, which has stiff polymer chains, has a higher IDT and T_g than those of the other polymers. The glass transition is observed as a combined effect of the free volume associated with the side chains, which hinder the intermolecular dipolar interactions and the stiffness of the molecular backbone. The degradation is observed as the combined effect of the hydrocarbon content and the stiffness of the molecular backbone.

Isothermal studies were performed on these polymers using DSC and TGA. It was found that the weight of the samples remains well above 98% of the initial weight in TGA and the heat supplied to the

samples remains fairly constant, within experimental error, in DSC. This suggests that the samples are thermally stable at the testing temperatures, as shown in Figure 10.

Mechanical properties

In the case of mechanical properties it was found that linear pentene polycarbonate, linear hexene polycarbonate, and linear octene polycarbonate, which have glass transitions in the subzero region, are mechanically very delicate at room temperature. The films prepared from these samples were so weak and flimsy that tensile testing on those films could not be conducted. These polymers will have applications not based on their mechanical properties but based on other properties such as adhesion, processibility, and thermal degradation.

The tensile properties of the remaining polymers, polyethylene carbonate, polypropylene carbonate, cyclohexene polycarbonate, and the terpolymer, were
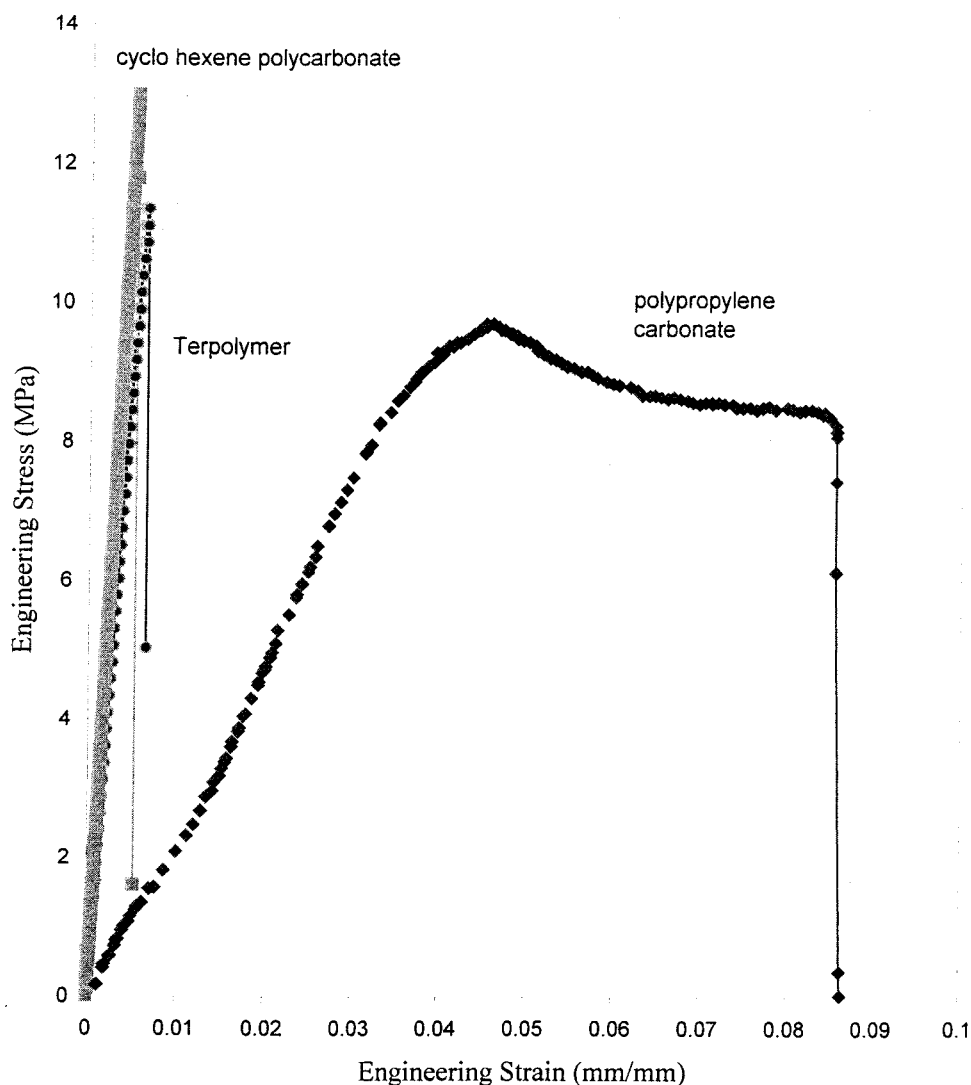
Figure 11 Representative stress–strain curves for aliphatic polycarbonates.

determined at room temperature. The representative engineering stress–strain curves for cyclohexene polycarbonate, terpolymer, polypropylene carbonate, and polyethylene carbonate are shown in Figures 11 and 12. The crosshead speeds used were as follows: terpolymer and cyclohexene polycarbonate at 1 mm/min, polypropylene carbonate at 10 mm/min, and polyethylene carbonate at different crosshead speeds.

It can be seen that the mechanical properties of the polymers are related to the glass-transition temperature, which is further related to the structure of the polymers. The elastic modulus of the polymers decreased from cyclohexene polycarbonate to terpolymer to polypropylene carbonate in the same order as their glass-transition temperatures. Cyclohexene polycarbonate and the terpolymer are brittle materials at room temperature and the strain at break was found to be less than 1%, whereas polyethylene carbonate behaves as an elastomeric material, with a strain at break greater than 600%.

The modulus of polyethylene carbonate was dependent on strain rate, as shown in Figure 12. It was observed that the polyethylene carbonate showed complete recovery to its initial length after removal of the load. It therefore has a great potential for use as a thermoplastic elastomer, which can be environmentally degraded. The average mechanical properties of the aliphatic polycarbonates are summarized in Table V.

There is a marked increase in the modulus and decrease in the strain at break from terpolymer to cyclohexene polycarbonate. The reason for this behavior is, again, the reduction in the chain stiffness in the molecules of the former attributed to incorporation of 20% polypropylene oxide during synthesis. Thus it is observed that the incorporation of flexible units in the main chain of the polymer also causes plasticization, similar to that by the flexible side chains in the other homologs of aliphatic polycarbonates.
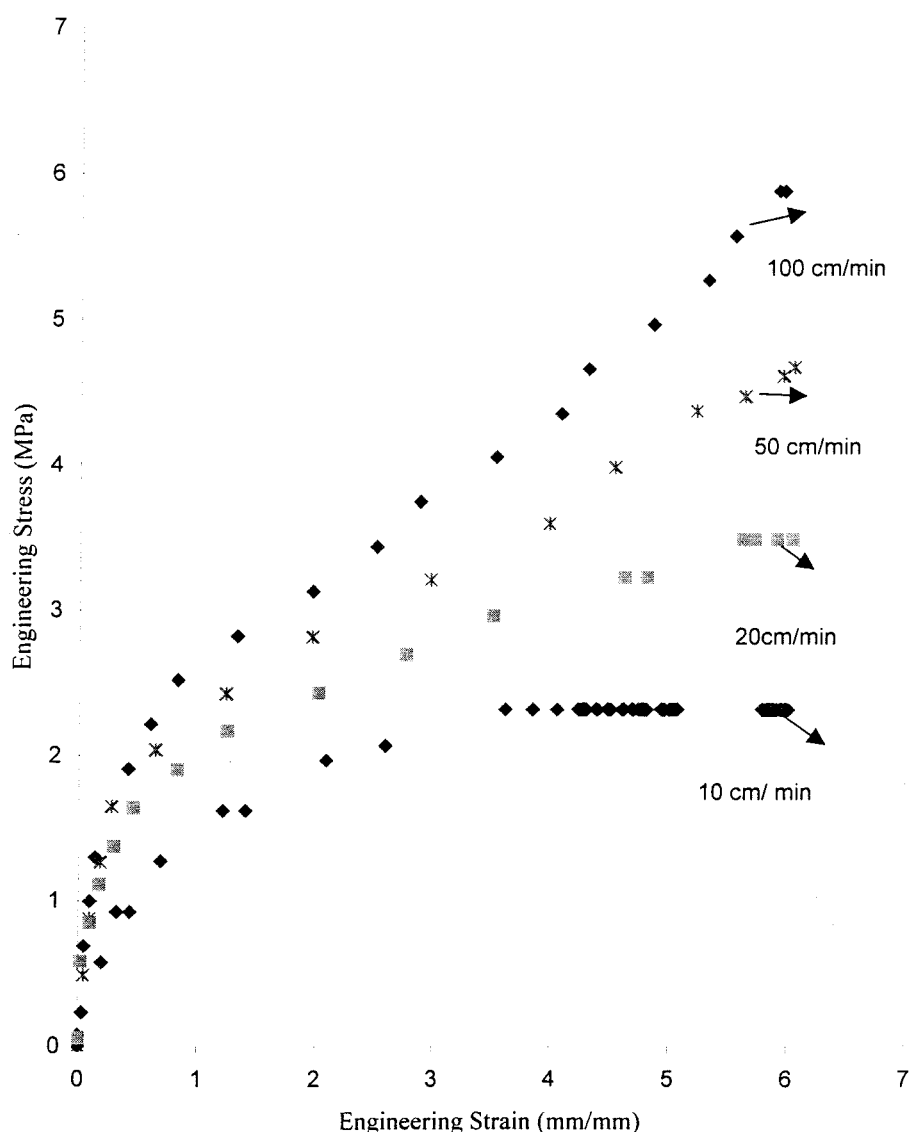
Figure 12 Representative stress–strain curves for polyethylene carbonate at different crosshead speeds.

CONCLUSIONS

It is concluded that aliphatic polycarbonates are a family of thermoplastics that can be tailor-made to yield polymers of desired thermal and mechanical

TABLE V
Average Mechanical Properties of Aliphatic Polycarbonates

Polymer	Modulus (MPa)	Tensile strength (MPa)	Strain at break (%)
Polyethylene carbonate	3–8	—	>600
Polypropylene carbonate	212	9	8
Terpolymer of CO_2, propylene oxide (20%), and cyclohexene oxide (80%)	2080	13.5	0.7
Poly(cyclohexene carbonate)	2460	11.8	0.5

behavior, depending on the specific application. Thermal properties such as glass-transition temperature (T_g) and initial decomposition temperature (IDT) depend on the length of the side chain, intermolecular dipolar interaction, hydrocarbon content of the repeat unit, and the stiffness of the backbone chain. These factors also affect the mechanical behavior of the polymers at room temperature. By addition of the third monomer, the chemical structure of the polymer is changed and a polymer with designed properties can be obtained. Studies of the effect of the chemical structure and the molecular weight distribution on the processing behavior and the rheological properties of these polymers are under way. Studies are also being planned regarding the effect of chemical crosslinking, blending, complexation, and IPN formation with other polymers on the physical properties of these polymers.

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