The Effects of Chemical Structure on the Shear Rheology of Aliphatic Polycarbonates

Sudhir D. Thorat,[1] P. J. Phillips,[2] Viktor Semenov,[3] Andre Gakh[4]

[1]*420, Dougherty Engineering Building, Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996, U.S.A.*
[2]*609, Dougherty Engineering Building, Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996, U.S.A.*
[3]*Zelinsky Institute of Organic Chemistry, Leninsky Prospekt 47, 117913 Moscow, Russia*
[4]*Science & Technology Advisor, Lockheed Martin Energy Systems, U.S. Department of Energy, 1000 Independence Ave SW, Washington, DC 29585, U.S.A.*

Received 17 November 2003; accepted 13 February 2004
DOI 10.1002/app.20457

ABSTRACT: Aliphatic polycarbonates are a relatively new class of polymer, which are characterized by an instability at the functional group, which makes them easily degraded and capable of biodegradation; as such, they constitute a potentially powerful group of polymers for exploitation in green technology. Rheological properties in shear flow are presented for the seven following different aliphatic polycarbonate samples: polyethylene carbonate, polypropylene carbonate, linear pentene polycarbonate, linear hexene polycarbonate, linear octene polycarbonate, cyclohexene polycarbonate, copolymer of propylene oxide (20%), and cyclohexene oxide (80%), using parallel plate rheometry. No studies of the rheological properties of aliphatic polycarbonates have been reported in the literature to date. The steady-state and the dynamic properties of these new polymers are investigated, and the resulting flow curves and the dynamic relaxation spectra of the aliphatic polycarbonate melts are presented. One of the major problems encountered in trying to characterize the melt rheology and relate behavior to the underlying molecular structure is the instability of the polymers. Because of this, a narrow processing window is present for each polymer, and it makes it impossible to compare all polymers at a constant temperature or range of temperatures in the melt. Nevertheless, some progress can be made. In all cases, the rheological response is discussed in terms of molecular characteristics, in particular, the length of the side chain and the molecular weight distribution. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 534–544, 2004

Key words: aliphatic polycarbonates; length of side chain; flow curve; dynamic relaxation spectrum; molecular weight distribution

INTRODUCTION

The shear and elongational rheological behavior of polyethylenes has been extensively studied with reference to both physical variables and structural parameters[1,2] and considerable knowledge now exists for this group of polymers. Aliphatic polycarbonates are recent polymers with growing applications in a number of fields.[3–9] It is expected that these polymers will be subjected to a number of different polymer processing operations to meet new applications; hence, the flow behavior of this new family of polymers is of great importance in determining their processing characteristics. Indeed, because of their sensitivity to both temperature and environment, they are potential replacements for several common polymers which are not degraded in the environment or which degrade very slowly. A study of the structure–property relations has already been published,[10] but the rheological characteristics are not yet in the literature.

Study of the rheological behavior is limited by the glass transition temperature and the onset of degradation, caused by the instability of the carbonate group. As has been demonstrated,[10] this results in narrow temperature windows for each polymer for both study and processing of the polymers in the molten state.

Aliphatic polycarbonates used in this research are essentially defective alternating copolymers formed by ring-opening polymerization of terminal epoxides with CO_2 by using zinc adipionate as catalyst [patented process of Empower Materials (formerly PAC Polymers Inc.)]:

Correspondence to: P. J. Phillips, Dept. of Chemical & Materials Engineering, University of Cincinnati, P.O. Box 210012, Cincinnati, OH 45221-0012.

Contract grant sponsor: Department of Energy, through Lockheed Martin Energy Systems; contract grant number: DE-AC05-84OR21400.

Journal of Applied Polymer Science, Vol. 93, 534–544 (2004)

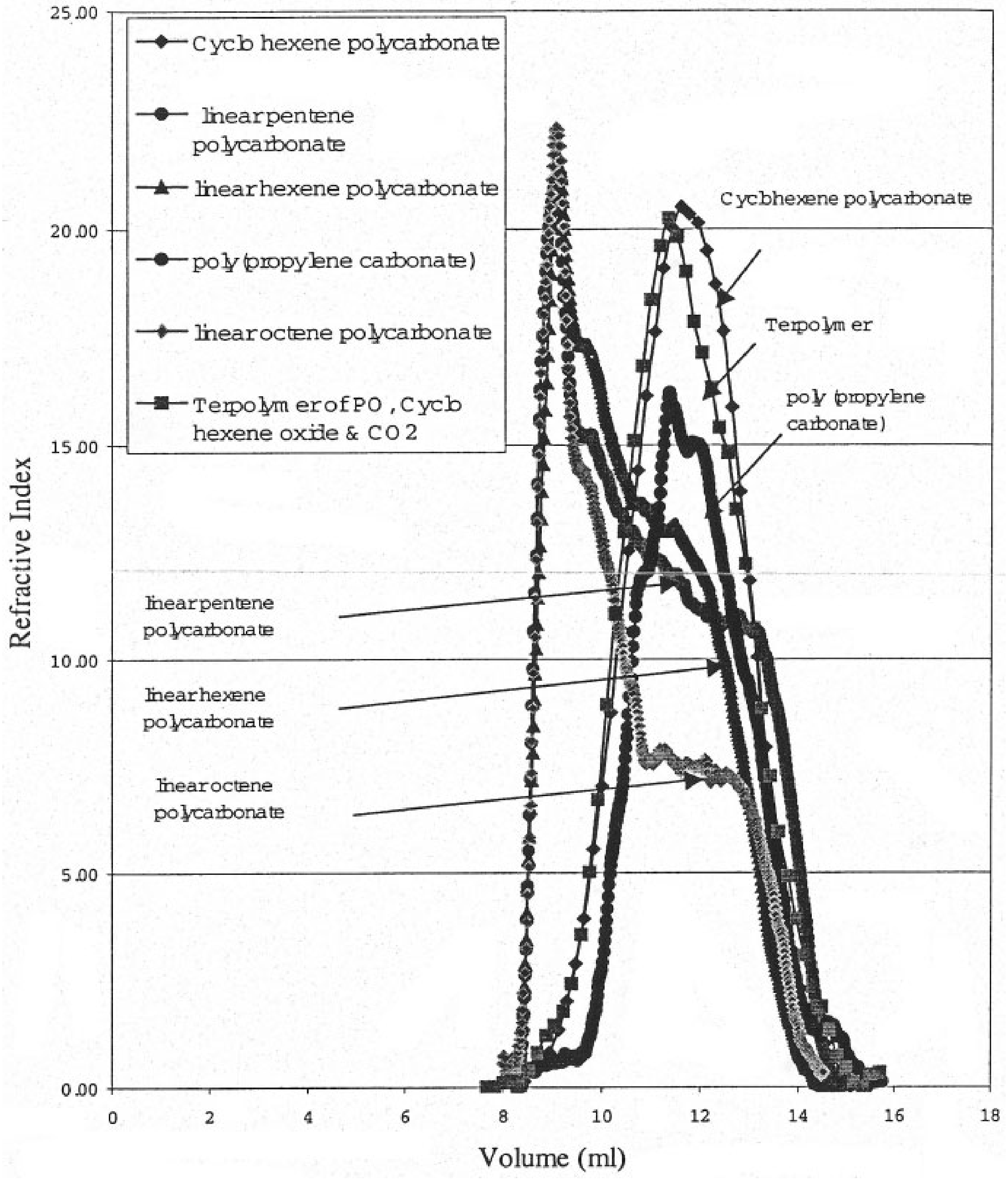
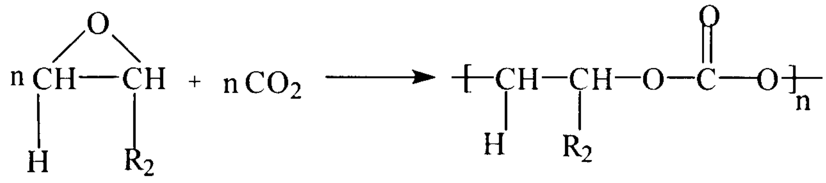


Figure 1 GPC curves for aliphatic polycarbonates.



$$n\,\underset{H}{CH}\overset{O}{—}\underset{R_2}{CH} + n\,CO_2 \longrightarrow \left[\underset{H}{CH}—\underset{R_2}{CH}—O—\overset{O}{\overset{\|}{C}}—O \right]_n$$

Different molecular structure polymers are synthesized by using different monomers. The alternating copolymerization gives rise to a side chain in each repeat unit of the polymer. It has been shown earlier[10] that these polymers contain ether groups resulting from a side reaction involving two or more epoxide monomers, using this method of synthesis. This results in the suppression of crystallinity and all the

TABLE I
Polystyrene equivalent molecular weights of aliphatic polycarbonates.

Polymer	M_w	M_n	PDI (polydispersity index)
Polypropylene carbonate	28,900	7540	3.83
Linear pentene polycarbonate	44,400	7500	5.13
Linear hexene polycarbonate	45,500	9490	4.79
Linear octene polycarbonate	49,400	10500	4.70
Terpolymer of CO_2, propylene oxide (20%) and cyclohexene oxide (80%)	35,200	8680	5.27
Poly(cyclohexene carbonate)	33,800	7980	4.23

polymers are amorphous. The aim of this work was to present the shear thinning behavior and the dynamic relaxation properties of seven aliphatic polycarbonate samples with differing chemical structure. It was shown elsewhere[10] that these polymers can be tailored to give desired mechanical, thermal relaxation, and degradation properties by changing their molecular structure. The present work not only reveals the fundamental rheological properties of these polymers but also begins to elucidate the relationship between these properties and the structure of the polymers, which is important for the desired processing behavior.

EXPERIMENTAL

Materials

The materials employed in this work were the following seven aliphatic polycarbonates: polyethylene carbonate, polypropylene carbonate, linear pentene polycarbonate, linear hexene polycarbonate, linear octene polycarbonate, cyclohexene polycarbonate, copolymer of propylene oxide (20%), and cyclohexene oxide (80%). The sample code includes the monomer type with the number of carbon atoms followed by the word PC. The synthesis of the polymers was carried out by V. Semenov and described earlier.[10]

Experimental procedures

Molecular weight characterization

Gel permeation chromatography (GPC) was performed by using a Waters 590 model with μ-Styragel columns in THF as solvent. The solutions with a concentration of ~ 9 mg/5 mL were used. The 200-μL solution was injected in the column with a flow rate of 1 mL/min at 40°C. The column was calibrated by using polystyrene standards of molecular weights 240K, 169K, 95K, 50K, 17.5K, and 3.5K under the same conditions. The technique measures the differential refractive index of the emerging solution.

Rheological studies

A Rheometric Scientific ARES parallel plate rheometer was used to study the rheological behavior of the polymers, using 25-mm-diameter plates. Amplitude sweep, frequency sweep, and flow curve experiments were performed. The samples were cut from the sheets of ~ 1 mm thickness and pressed between the parallel plates to ensure that there was no air gap left between the plates. As has been stated earlier, the possible temperature range that can be used is controlled by the glass transition temperature of the individual polymer and its degradation temperature. The polycarbonates based on linear pentene, linear hexene, and linear octene were tested at 140°C; poly(ethylene carbonate) was tested at 150°C, and poly(propylene carbonate) was tested at 180°C. The terpolymer and cyclohexene polycarbonate were tested at 210°C. The temperatures were decided on the basis of previously reported glass transition and thermal degradation studies and the melt flow index studies of the polymers.

RESULTS AND DISCUSSION

Non-Newtonian shear thinning behavior of a polymer is studied by using the change in viscosity against the shear rate, which is varied by changing the frequency of rotation of the parallel plate.

Before studying the shear-thinning behavior, GPC was used to find the molecular mass distribution of the aliphatic polycarbonates. The combined curves are given in Figure 1. Although the absolute values of the molecular weights cannot be obtained just by using GPC alone, the polystyrene equivalents of the molecular weights were calculated and are presented in Table I. It can be seen from the GPC curves that linear pentene, hexene, and octene polycarbonates do not have a normal distribution of molecular weight. It was found that the solutions of these polymers in THF are stable with no precipitation occurring after the solution was allowed to stand for 7 days. Polyethylene carbonate was found to be insoluble in THF and hence its molecular weight distribution could not be obtained.

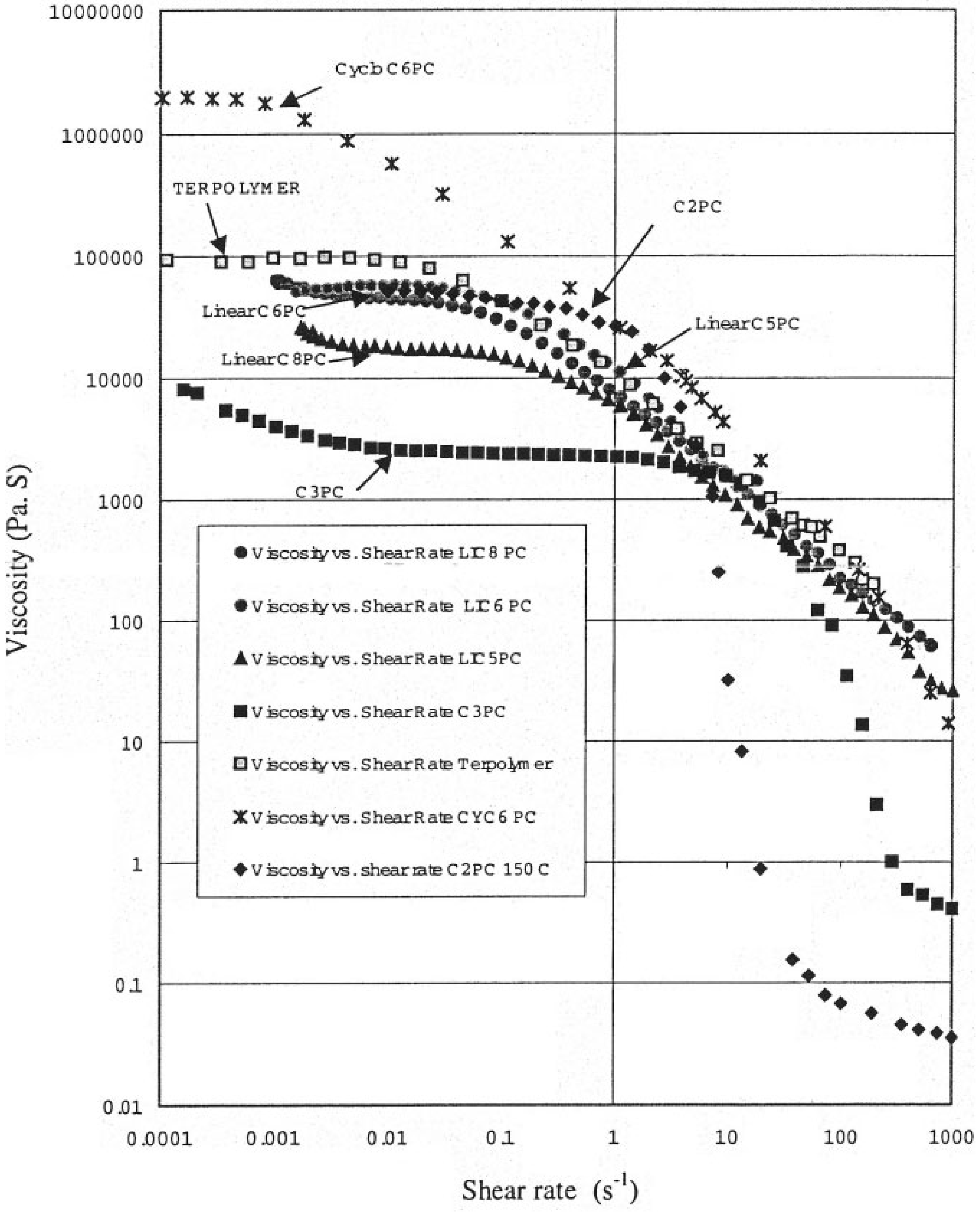


Figure 2 Flow curves for all the aliphatic polycarbonates.

From the GPC curves for linear pentene, hexene, and octene polycarbonates, it is seen that these polymers have a significant population of high molecular weight molecules. There is also a considerable population of low molecular weight molecules and the distribution tends to be bimodal and broad. The molecular mass for the four remaining polymers show normal and narrow distributions. The apparent viscosity of the aliphatic polycarbonates is plotted against the shear rate in Figure 2. Because the processing temperatures of aliphatic polycarbonates are different, the flow curves for these polymers were obtained at their processing temperatures rather than at a constant temperature.

Linear pentene, hexene, and octene polycarbonates were tested at 140°C, polyethylene carbonate at 150°C, polypropylene carbonate at 180°C, while the terpolymer and cyclohexene polycarbonate were tested at 210°C.

Although for comparison purposes the flow curves for the polymers should be obtained at the same temperature, we assume that the activation energy is not

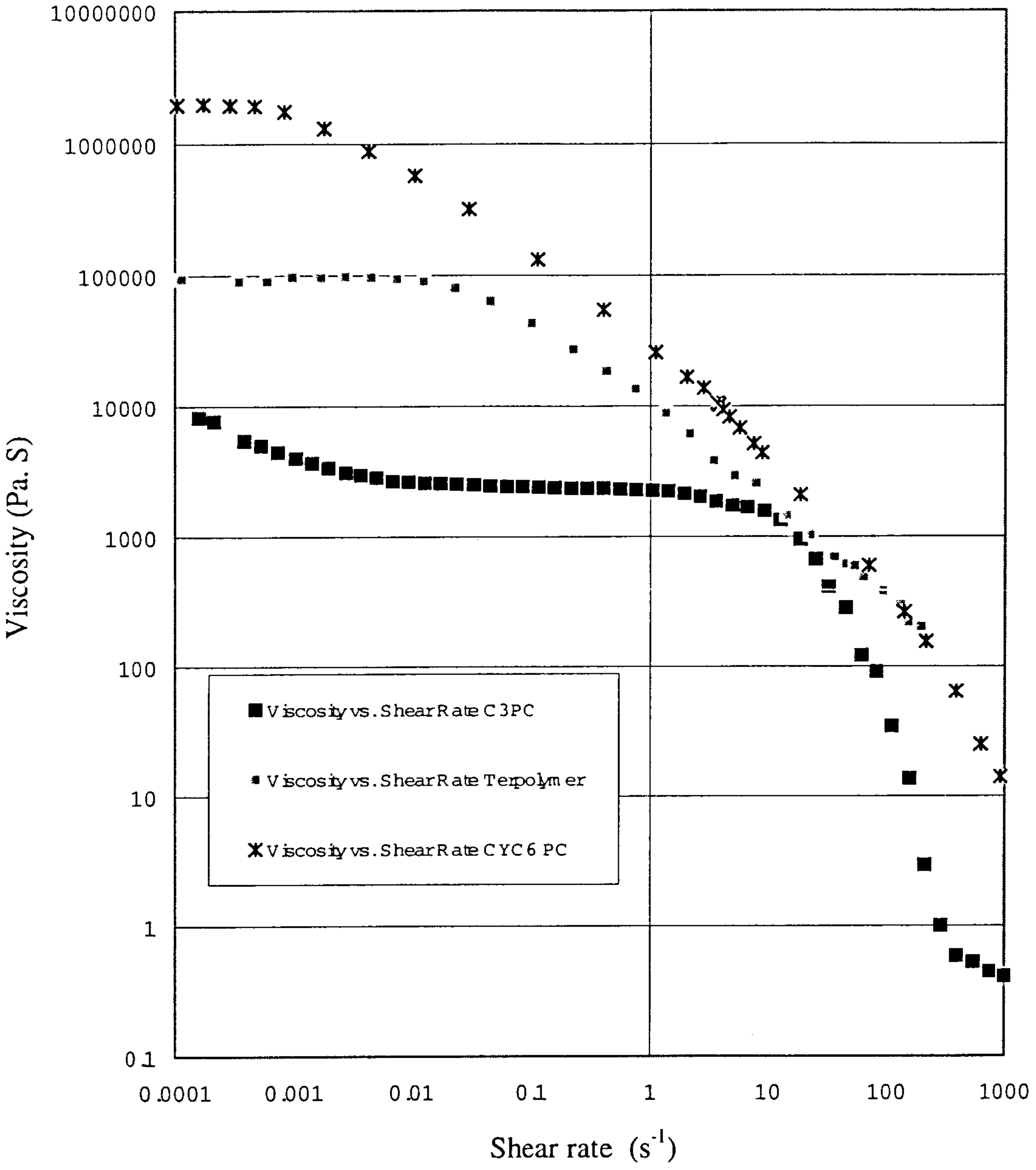
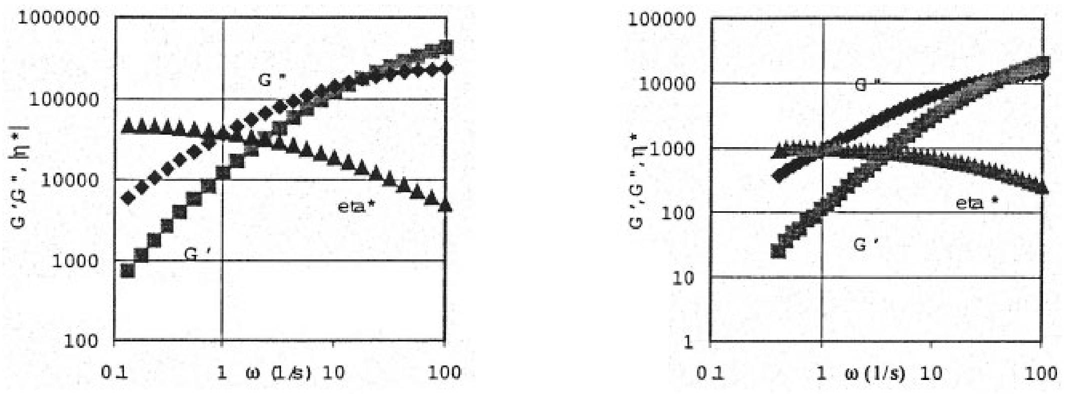


Figure 3 Flow curves for polycarbonate, cyclohexene polycarbonate, and the terpolymer.

a strong function of shear rate for these polymers in the given temperature range, and that the shape of flow curves will not change drastically with temperature. With these assumptions, we can begin to look for relations between the molecular structure and the rheological behavior. Remarkably, some clear trends do emerge. The positive trends observed are probably a result of the polymers being studied at approximately the same number of degrees above their glass transition temperatures.

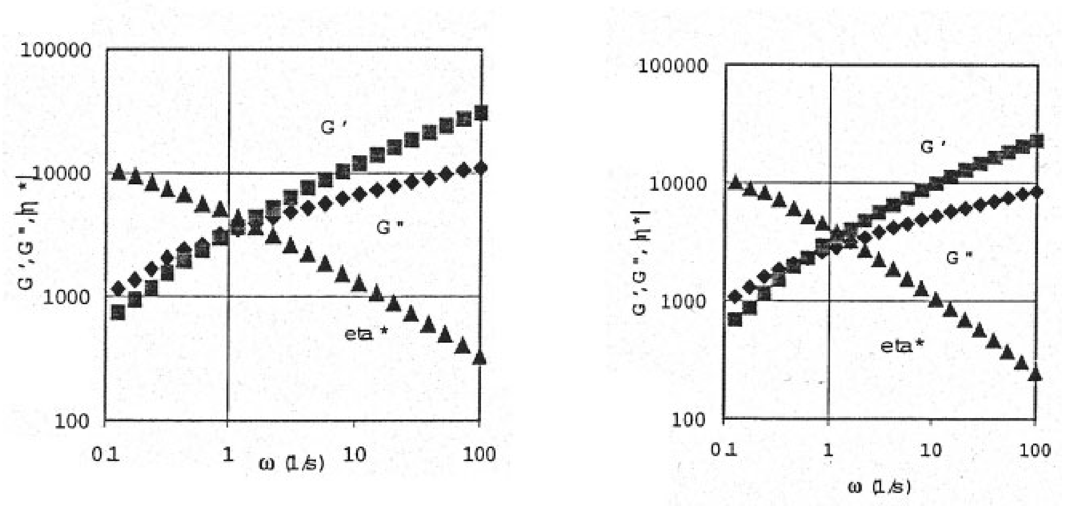
From Figure 2, it can be seen that polyethylene carbonate and polypropylene carbonate show highly shear thinning behavior. Moreover, the critical shear rate at which the shear thinning starts is large compared to the other polymers. Polyethylene carbonate shear thins to a very low viscosity at higher shear rates. It was confirmed that there is no mechanical degradation occurring in the polymer because the recovery of the viscosity at the lower shear rates could be observed in the same polymer sample.

Such a high degree of shear thinning is hypothesized as occurring because of a breakdown of the strong secondary intermolecular bonds existing in polar molecules at higher shear rates. Polyethylene carbonate and polypropylene carbonate have small pendant side chains in the repeat unit and hence can have strong intermolecular bonds. These bonds are broken due to the high shear and the viscosity of the polymers



a) Polyethylene carbonate

b) Polypropylene carbonate



c) Linear pentylene polycarbonate

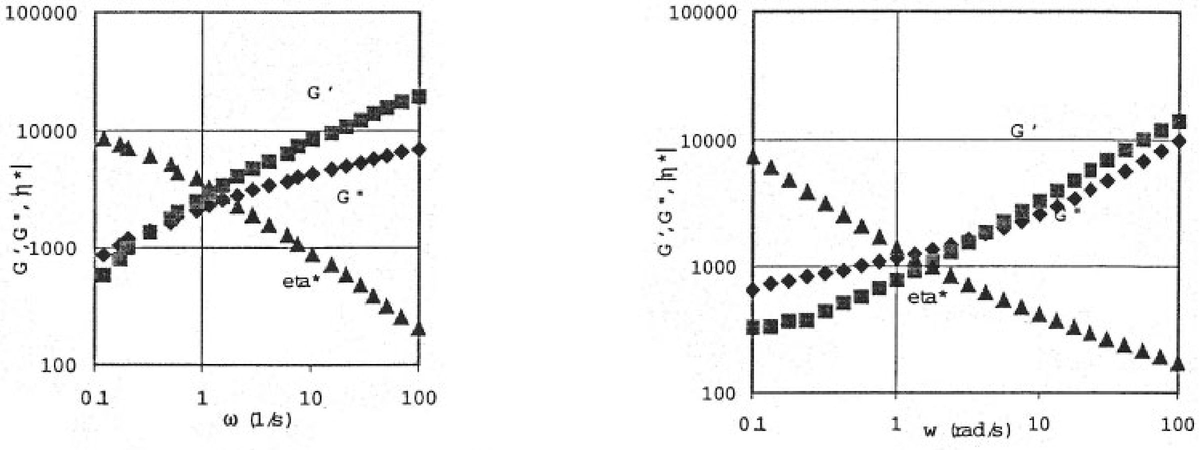
d) Linear hexene polycarbonate

Figure 4 Experimental dependences of the components of dynamic shear modulus and complex viscosity on frequency (G' and G'' are in Pa; $|\eta^*|$ is in Pa S).

decreases drastically beyond a critical shear rate. As the length of the side chain increases, the intermolecular interactions are hindered and the molecules are pushed apart. Thus, molecules can slip past one another more easily and cause shear thinning to occur at lower shear rates.

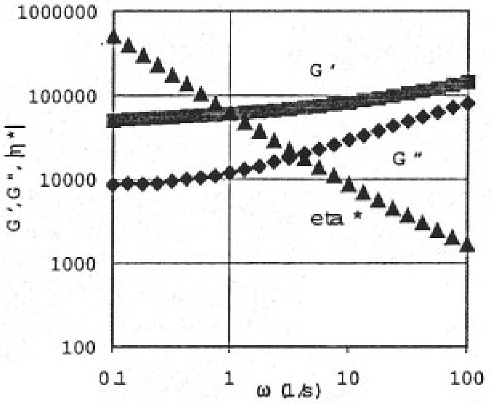
In the case of cyclohexene polycarbonate and the terpolymer, although the molecular weight distribution is similar to that of polypropylene carbonate, the flow curves are quite different, presumably due to the effect of the bulky cyclohexane group in the main chain. As expected, the terpolymer flow properties (such as onset of shear thinning, zero shear viscosity) fall in between cyclohexene carbonate and polypropylene carbonate as shown by separate flow curves in Figure 3. Because of the high glass transition temperatures, the processing temperatures for cyclohexene polycarbonate and the terpolymer are higher than for the other aliphatic polycarbonates. Even at the highest testing temperatures, these two polymers show the highest zero shear viscosity of the series because of the stiff polymer chains.

In the case of linear pentene, hexene, and octene polycarbonates, in addition to the effect of longer side chains, it is also necessary to consider the effect of molecular weight distribution. In these polymers, even though the side chains contain merely 3, 4, and 6 C-atoms, due to the alternating copolymerization,



e) Linear octene polycarbonate

f) Terpolymer



g) Cyclohexene polycarbonate

Figure 4 (*Continued from the previous page*)

each repeat unit will have a side chain and hence the effect of these side chains on hindering the intermolecular dipolar interactions of adjacent groups will be considerable. In addition, these polymers have a significant population of high molecular weight molecules, which gives rise to non-Newtonian behavior at lower shear rates, as explained earlier. This can be observed clearly in Figure 2. The shear rate corresponding to the onset of shear thinning increases from linear octene polycarbonate to linear hexene polycarbonate to linear pentene polycarbonate. However, there is no significant difference in the rate of shear thinning in these three polymers. These polymers do not undergo high shear thinning, as polyethylene carbonate and polypropylene carbonate, presumably, because of the presence of high molecular weight molecules, which dominates the rheological behavior at higher shear rates.

The viscoelastic properties of the polymers were obtained in the dynamic oscillatory mode of the rheometer. First of all, the range of strain or amplitude for the linear viscoelastic behavior of the polymer was ascertained by using the amplitude or strain sweep. After choosing a certain strain in the linear viscoelastic region of the polymer, a frequency sweep was performed in which the frequency of oscillation was varied at constant amplitude. The plots of G', G'', and complex viscosity $|\eta^*|$ are shown in Figure 4.

Consideration of the dynamic characteristics of the polymer melts makes it possible to classify their relaxation states at temperatures above the glass transition temperature. The low-frequency region corresponds to the fluid state; the plateau region of $G'(\omega)$ corresponds to the rubber-like state of linear polymers, where they are not able to flow, and the transition from one state to another takes place when the crossover of $G'(\omega)$ and $G''(\omega)$ curves takes place. At still higher frequencies, the transition to the glassy state of the polymer takes place. The dynamic method of studying the relaxation properties of polymers makes

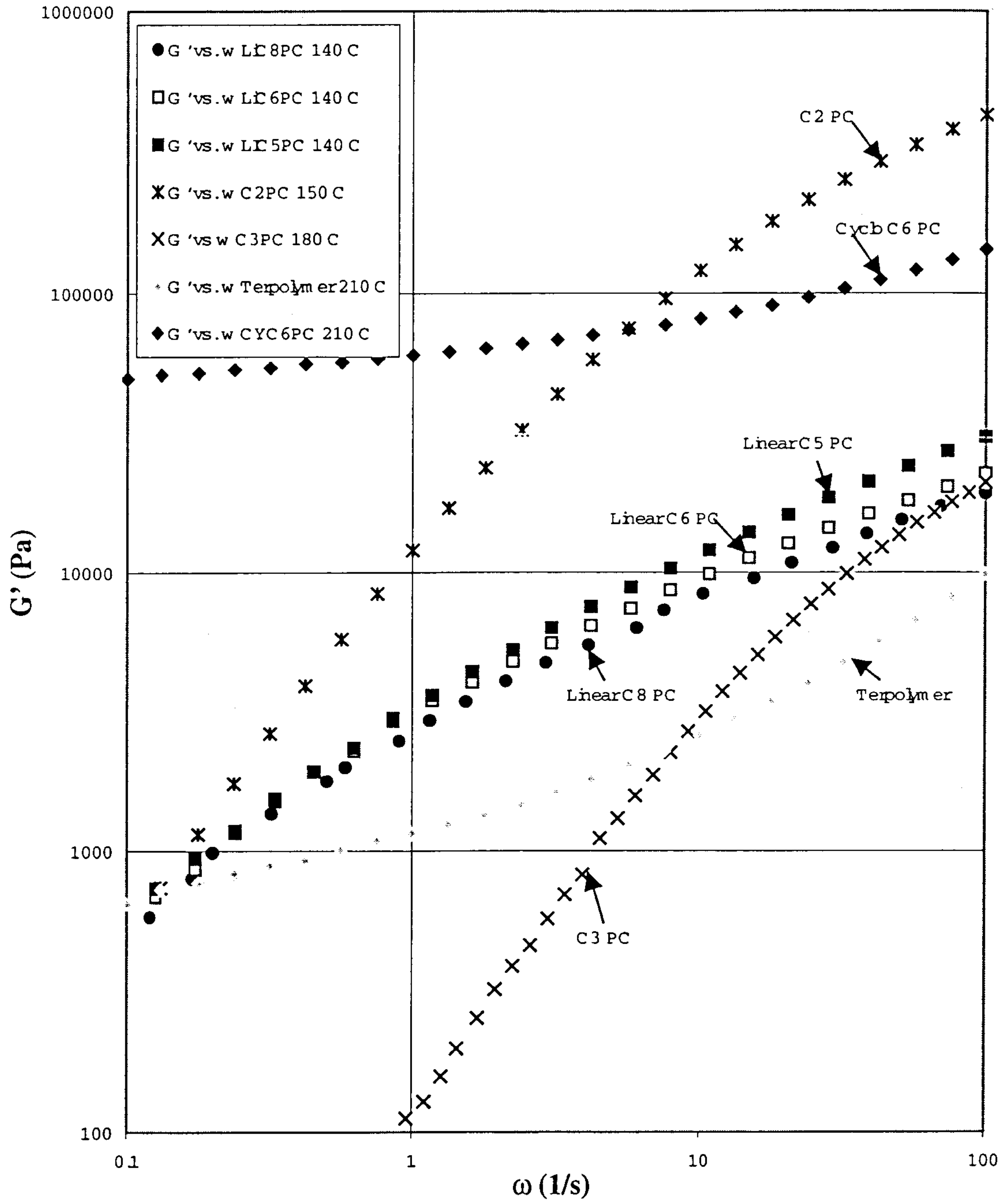


Figure 5 *G'* versus frequency for aliphatic polycarbonates.

it possible to determine the frequency regions corresponding to the transition of the polymers from the fluid state to rubbery, leathery, and glassy states.

The transition frequencies increase with increasing temperature for a given polymer. The structure of the polymer affects the entanglements, which further affects the dynamic relaxation and viscoelastic properties of the polymeric chains. When the elements forming the fluctuating entanglement network are subjected to mechanical action, the most important parameter is the average lifetime of a junction, or the relaxation time. If the relaxation time is very short, the structural units appear to be absolutely nonlinked; they slip freely at the junctions and the system behaves as a typical liquid. If the time is infinitely long, the polymer is capable of retaining strains and stresses for an infinitely long time. In aliphatic polycarbonates, the highly shear thinning polymers, polyethylene carbonate, and polypropylene carbonate show higher relaxation frequencies, or lower relaxation times, for the fluid to rubbery transition. The subzero glass transition polymers, linear pentene, linear hexene, and lin-

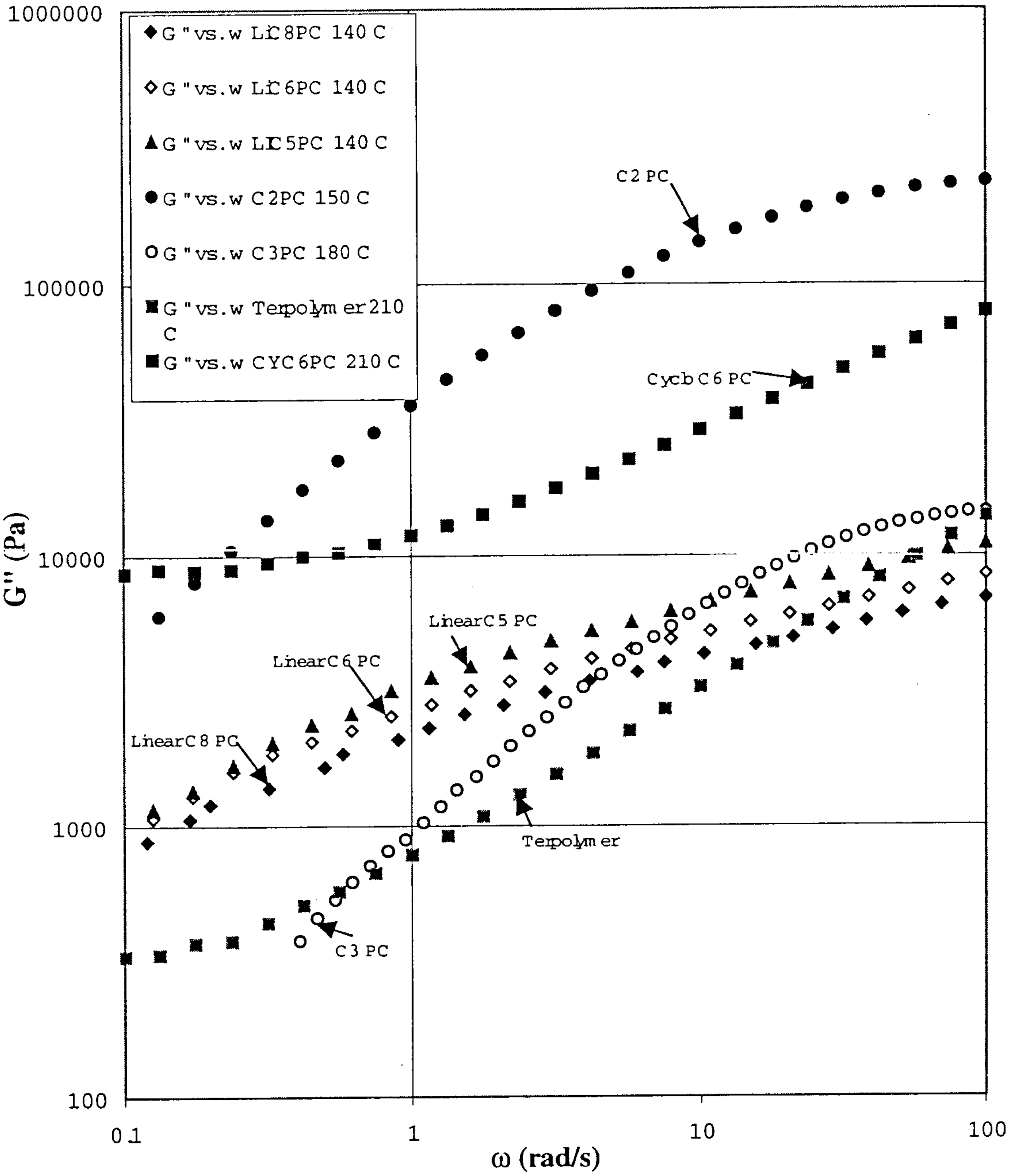


Figure 6 *G″* versus frequency for aliphatic polycarbonates.

ear octene polycarbonates show higher relaxation times. In a polydisperse system, it is necessary to consider the effect of each fraction of the molecular weight on the relaxation time. These polymers have a significant population of high molecular weight molecules, which must be dominating the rheological properties, and hence, leading to higher relaxation times. Also, the lower testing temperature gives rise to a lower relaxation frequency or to higher relaxation times.

In the case of the stiff polymers, cyclohexene polycarbonate, and the terpolymer, high relaxation times are obtained. The relaxation frequency of cyclohexene polycarbonate is lower than 0.1 s^{-1} and the polymer is in the elastic region over the entire frequency range studied (0.1–100 s^{-1}). This is important because the polymer is tested at 210°C (i.e., the maximum temperature in this series), and it still has the highest relaxation time. The lowest relaxation times being observed for polyethylene carbonate and polypropylene carbonate implies that the chains are nonlinked and slip freely at the junctions; however, the reason for this behavior is not clearly understood.

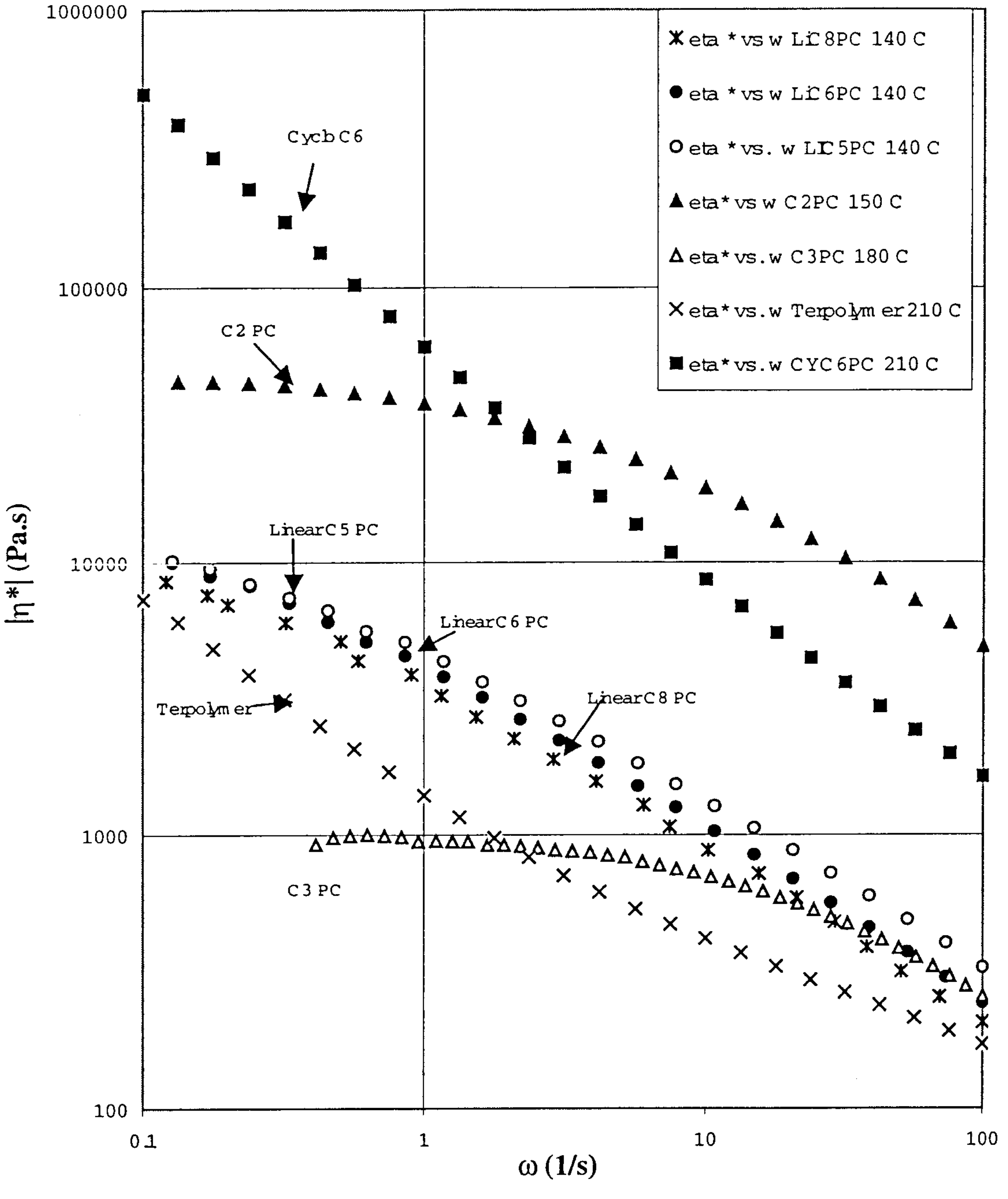


Figure 7 Magnitude of complex viscosity versus frequency for aliphatic polycarbonates.

The individual plots of G', G'', and $|\eta^*|$ for all the polymers are shown in Figures 5 to 7. From these curves, it is clear that the rheological behavior of given samples of aliphatic polycarbonates can be divided into the three following categories: (1) Polyethylene carbonate and polypropylene carbonate form one group, which shows high shear thinning behavior and low relaxation times. (2) Addition of the longer side chains gives rise to another group of polymers comprising linear pentene, linear hexene, and linear octene polycarbonates. This group shows lower steady-state viscosities and critical shear rates due to the presence of side chains; however, due to the presence of significant population of high molecular weight molecules, they show comparatively less shear thinning behavior and higher relaxation times. (3) The third group consists of cyclohexene polycarbonate and the terpolymer, which show high steady-state viscosities and high relaxation times due to the stiffness of the polymer chains.

CONCLUSION

The rheological behavior of aliphatic polycarbonates is significantly affected by the chemical structure (viz.

the length of the side chain and the molecular weight distribution). All the polymers were found to be shear thinning. Polypropylene carbonate and polyethylene carbonate were found to be highly shear thinning, making them ideal candidates for injection molding and extrusion operations. Linear pentene, linear hexene, and linear octene polycarbonates were found to have a significant population of high molecular weight molecules and hence, they shear thin at a comparatively slower rate. The zero-shear viscosities of cyclohexene polycarbonate and the terpolymer were the highest among all aliphatic polycarbonates (although they were tested at the highest temperature). The high zero-shear viscosity with apparent good melt strength and less die swell (as observed in melt flow indexer) makes cyclohexene polycarbonate and the terpolymer good candidates for blow-molding applications.

Dynamic rheological spectra of the polymers show that the relaxation times for linear pentene, linear hexene, and linear octene polycarbonates are higher because of the presence of significant populations of high molecular weight molecules. Cyclohexene polycarbonate and the terpolymer also have large relaxation times because of stiff chains. Polyethylene carbonate and polypropylene carbonate exhibit the smallest relaxation times. From the combined dynamic rheological spectra of polycarbonates, it is concluded that, based on rheological properties, aliphatic polycarbonates can be divided into three groups. From the variation of G', G'', and η^* with frequency, we see that (1) linear pentene, linear hexene, and linear octene polycarbonates form one group; (2) polyethylene carbonate and polypropylene carbonate form the second group; and (3) terpolymer and cyclohexene polycarbonate form the third group. Thus, these polymers can be tailor-made to produce the desired rheological behavior for a given process.

This research was supported by the Department of Energy, through Lockheed Martin Energy Systems subcontract 4500005290 of prime contract DE-AC05-84OR21400. Extensive discussions with Prof. John Collier are gratefully acknowledged.

References

1. Valenza, A.; La Mantia, F. P.; Acierno, D. Eur Polym Mater 1988, 24 (1), 81.
2. Acierno, D.; La Mantia, F. P.; Romanini, D.; Savadori. A. Rheol Acta 1985, 24, 566.
3. Inoue, S. Chemtech 1976, 6 (9), 594.
4. Christel, R.; Schimmel Karl-Heinz, O. L. Ger. Pat. DE 1,975,028, 1999.
5. Christel, R.; Schimmel Karl-Heinz, O. L. Ger. Pat. DE 19,849,186, 1999.
6. Xiaoguang, Y.; Yuhui, H.; Guo, L.; Bing, L.; Mingcai, C.; Hao, P.; Shulu, Z.; Liban, C. Chin. Pat. CN 1,176,269, 1998.
7. Liben, C. Polym Bull (Beijing) 1999, 3 (9), 128.
8. Suyama, T.; Tokiwa, Y. Enzyme Microb Technol 1997, 20, 122.
9. Coates, G. W.; Cheng, M.; Lobkovsky, E. B. J Am Chem Soc 1998, 120, 11018.
10. Thorat, S. D.; Phillips, P. J;, Semenov, V.; Gakh, A. J Appl Polym Sci 2003, 89, 1163.