Investigation of side-chain crystallization and thermotropic behavior is now on progress.

References and Notes

(1) Hakomori, S. *Sci. Am.* **1986,** *254* (No. 5), 32.
(2) *Bacterial Lipopolysaccharides*; Anderson, L., Unger, F. M., Eds.; ACS Symposium Series 231; American Chemical Society; Washington, DC, 1983.
(3) Hayes, M.; Nestaas, E.; Hrebenar, K. *CHEMTECH* **1986,** 239.
(4) Goodby, J. W. *Mol. Cryst. Liq. Cryst.* **1984,** *110,* 205.
(5) Jeffrey, G. A. *Mol. Cryst. Liq. Cryst.* **1984,** *110,* 221.
(6) Jeffrey, G. A. *Acc. Chem. Res.* **1986,** *19,* 168.
(7) Michel, H. *Trends Biol. Sci.* **1983,** *8,* 56.
(8) Kawabata, Y.; Matsumoto, M.; Tanaka, M.; Takahashi, H.; Irimatsu, Y.; Tamura, S.; Tagaki, W.; Nakahara, H.; Fukuda, K. *Chem. Lett.* **1986,** 1933.
(9) Kawaguchi, T.; Nakahara, H.; Fukuda, K. *J. Colloid Interface Sci.* **1985,** *104,* 290.
(10) Bader, H.; Ringsdorf, H.; Skura, J. *Angew. Chem., Int. Ed. Engl.* **1981,** *20,* 91.
(11) Fuhrhop, J.-H.; David, H.-H.; Mathieu, J.; Liman, U.; Winter, H.-J.; Boekema, E. *J. Am. Chem. Soc.* **1986,** *108,* 1785.
(12) Pfannemuller, B.; Welte, W. *Chem. Phys. Lipids* **1985,** *37,* 227.
(13) Fuhrhop, J.-H.; Schnieder, P.; Rosenberg, J.; Boekema, E. *J. Am. Chem. Soc.* **1987,** *109,* 3387.
(14) Sunamoto, J.; Iwamoto, K. *Therapeutic Drug Carrier Systems*; CRC Press: Boca Raton, FL, 1986; Vol. 2, p 117.
(15) Sunamoto, J.; Sato, T.; Hirota, M.; Fukushima, K.; Hiratani, K.; Hara, K. *Biochim. Biophys. Acta* **1987,** *898,* 323.
(16) Sunamoto, J.; Sakai, K.; Sato, T.; Kondo, H. *Chem. Lett.* **1988,** 1781.
(17) Schuerch, C. *Adv. Carbohydr. Chem. Biochem.* **1981,** *39,* 157.
(18) Sumitomo, H.; Okada, M. *Ring-Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier Applied Science: London, 1984; Vol. 1, p 229.
(19) Kochetkov, N. K. *Tetrahedron* **1987,** *43,* 2389.
(20) Kobayashi, K.; Sumitomo, H. *Nippon Kagaku Kaishi* **1982,** 1633.
(21) Kobayashi, K.; Sumitomo, H. *Polym. J. (Tokyo)* **1984,** *16,* 297.
(22) Kobayashi, K.; Sumitomo, H.; Ichikawa, H. *Macromolecules* **1986,** *19,* 529.
(23) Ichikawa, H.; Kobayashi, K.; Sumitomo, H. *Makromol. Chem.* **1988,** *189,* 1019.
(24) BeMiller, J. N.; Wing, R. E.; Meyers, C. Y. *J. Org. Chem.* **1968,** *33,* 4292.
(25) BeMiller, J. N.; Muenchow, H. L. *Carbohydr. Res.* **1973,** *28,* 253.

Communications to the Editor

Time Dependence of the Storage Modulus of Polycarbonate following Temperature Jumps within the Glassy State

Introduction. It has long been known that the physical properties of an amorphous polymer in the glassy state depend on its thermal and mechanical histories. An early detailed study was made by Kovacs,[1,2] who quenched specimens from the equilibrium rubbery state to the glassy state and then monitored the slow but continuous decrease in volume under isothermal conditions. (The volume never reaches a constant value in any ordinary experimental time, except when the temperature is no more than 15 or possibly 20 °C below T_g.) The decrease in volume is accompanied by a progressive reduction in the mobility of short molecular segments that produces a continuous increase in the retardation times. Consequently, following a quench from above T_g, the viscoelastic and other physical properties become time dependent under isothermal conditions, as shown by a number of studies.[2-5] Struik[4,5] has termed such phenomena physical aging, a term selected because the aging can be reversed by heating a specimen above T_g or it can be partially, if not completely, reversed by subjecting the specimen to a mechanical deformation.[4,6]

At part of his studies, Kovacs observed a phenomenon commonly termed a memory effect.[2,7] Specifically, after volume recovery (volume decrease) has occurred for a significant period at temperature T_1 that is substantially below T_g, the temperature is increased stepwise to T^*, which is still below T_g. At T^*, the volume first increases for a period (after temperature equilibrium has been established), then it passes through a maximum, and finally it decreases, eventually joining the original volume–time curve. Similar behavior has also been found during the intermittent measurement of creep curves, each for a relatively short period.[4,8] First, such curves were determined during physical aging at a relatively low temperature, reached by quenching the specimen from above T_g. Then, after a temperature jump to a higher temperature, which is still below T_g, the creep compliance, from the repeated measurements of short-term creep curves, was found to increase for a period, then to pass through a maximum, and finally to decrease continuously. These manifestations of the memory effect show that at least two, but in reality a broad distribution of, retardation times exist.

The present investigation of a well-annealed polycarbonate film was made to determine how its storage modulus in tension, E', depends on the elapsed time after a specimen has been subjected to two types of temperature jumps. For each jump, the initial and final temperatures are below T_g. Most previous studies of changes of mechanical properties during physical aging have been made on specimens that had been quenched from above to below T_g.

Experimental Section. A film of Bisphenol A polycarbonate 0.13-mm thick (Lexan from the General Electric Co.) was annealed for 1 h at 160 °C, then cooled slowly to 120 °C and annealed for 1 mo at this temperature, and finally cooled slowly to room temperature. This material was used in a study[9] at temperatures from −110 to +110 °C of the rate of physical aging of specimens maintained at a static elongation of 2.6%.

In the present study, a specimen was mounted in the tensile unit of a DMTA (dynamic mechanical thermal analyzer produced by Polymer Laboratories, Inc.) at room temperature, which is about 20 °C. The temperature was then increased at 20 °C/min to one of a series of temperatures above 20 °C. Each specimen was next subjected

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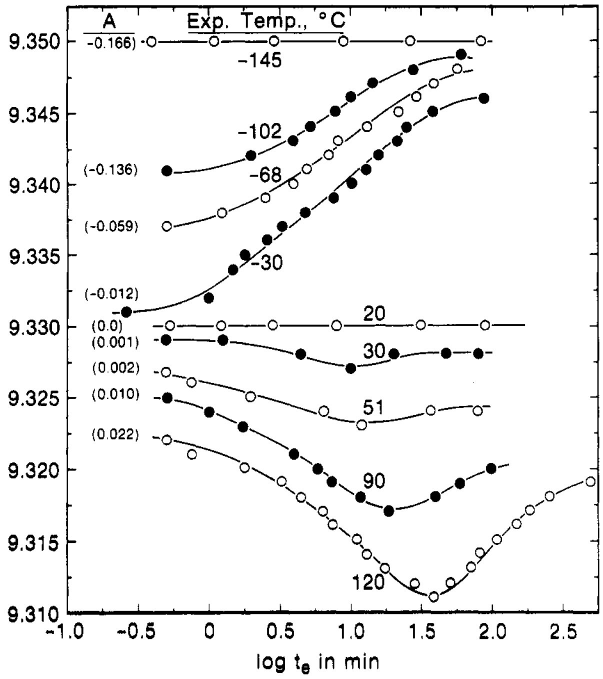

Figure 1. Time dependence of E' at 10 Hz determined at temperatures both above and below room temperature following quite rapid temperature changes from 20 °C, which was close to room temperature. The ordinate is $A + \log E'$; values of A are given in the figure.

to a static load sufficient to give initially a strain of 0.2%, and E' at 10 Hz was determined intermittently for 100 min or more. (The amplitude of the imposed sinusoidal strain was about 0.08%.) Similar measurements were made on specimens cooled rapidly from about 20 °C to each of a series of low temperatures. Also, a series of undeformed specimens were kept in the DMTA for 2 h at temperatures both above and below room temperature. Then the temperature of each specimen was changed rapidly to 30 °C, and E', again at 10 Hz, was measured intermittently during about 100 min.

Though the small static load applied to each specimen gave a small amount of creep during each measurement period, it is clear that the effect of this creep on E' is insignificant and does not affect in any way the conclusions reached.

Results and Discussion. Figure 1 shows the dependence of $\log E'$ on $\log t_e$, where t_e is the elapsed time beginning shortly after the test temperature was reached. (In Figure 1, the ordinate is $A + \log E'$ where the values of A are given in the figure. This procedure was used to separate the curves for clarity.) At 20 °C, considered to be room temperature, E' remained constant, as shown. But at the temperatures below 20 °C (-30, -68, and -102 °C), E' increased continuously during approximately 100 min, after which the measurements were terminated. The amount of the time-dependent increase of E' is significant but not unduly large. At -30 °C, for example, E' increased somewhat more than 3%. On the other hand, E' at -145 °C is time independent, which agrees with results from a previous study,[9] which showed that the physical aging of a specimen maintained at an elongation of 2.6% almost ceases at -110 °C. Also, it has been shown[10] that the low temperature peaks in G'' and $\tan \delta$ at 1 Hz occur at -100 °C, and so no aging would be expected at a temperature as low as -145 °C.

At each of the four temperatures above 20 °C, E' first decreases continuously, passes through a minimum, and finally increases with t_e, as shown in Figure 1. This behavior is another example of the memory effect, found by Kovacs[2,7] and by Struik[4,8] as mentioned in the Introduction. In contrast to the experiments by Kovacs and Struik, the temperature of specimens in this study was never above T_g.

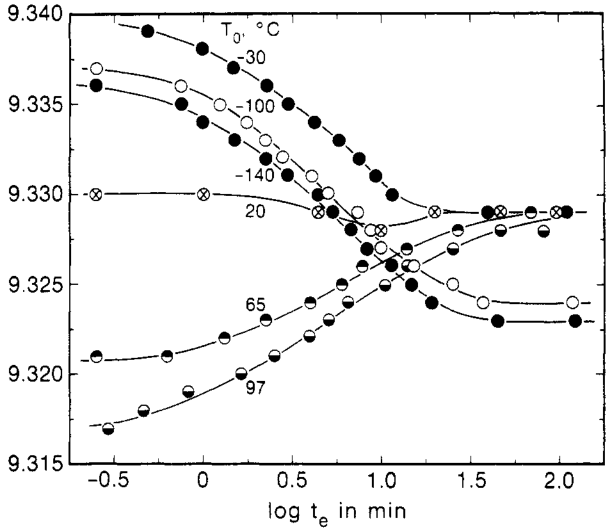

Figure 2. Time dependence of E' at 10 Hz and at 30 °C. The temperature given on each curve is that at which the specimen was annealed for 2 h. After that the temperature was changed rather rapidly to 30 °C.

In the second type of experiment, specimens mounted in the DMTA were annealed for 2 h at each temperature listed in Figure 2. Next, the temperature was changed rapidly to 30 °C, and then E' at 10 Hz was determined intermittently. Except for the specimen annealed at 97 °C, E' reached a constant value in approximately 100 min, or somewhat less, as shown in Figure 2. The terminal values of E' for the specimens annealed at -100 and -140 °C are smaller than those for the other specimens by about 1.3%. These differences are attributed to some unknown experimental error.

Other findings that E' at 10 Hz depends on time have been reported[11] in the last paragraph of that paper. As mentioned there, specimens of polycarbonate that had been keep at room temperature for many months were subjected in a Dynastat to a constant strain of 0.3% at three temperatures. At 90 and 110 °C, E' was determined intermittently for 8 h; at 70 °C, such measurements were made for 6 h. At 70, 90, and 110 °C, E' increased by 0.23, 0.30, and 0.94%. These values are rather small and differ from the behavior shown in the lower portion of Figure 1. The difference arises because in the study made with the Dynastat the time needed to reach the test temperature and the probable time before measurements were begun equals between 1 and 2 h or possibly more. So time-dependent changes in E' took place in large measure during the heating and soaking periods.

Conclusions. The present data on polycarbonate clearly show that E' depends on the elapsed time after a rapid temperature change within the glassy state. When the changed temperature was higher than room temperature, but still below T_g, E' first decreased with the elapsed time, passed through a minimum, and finally increased some before the experiment was terminated. This behavior is analogous to the memory effect, discussed in the Introduction. When the changed temperature is below room temperature, but not too far below, E' increased slowly for about 100 min. These results and those shown in Figure 2 demonstrate time effects that possibly have been noted on other occasions but not studied. It thus is to be expected that E' and tan δ, for example, will depend somewhat on time, as well as temperature and frequency, when they are determined on a polymer whose temperature has been changed rather quickly within the glassy state. The extent of the time dependence will depend on many factors, including the time to reach the desired test temperature, the time thereafter before measurements are begun, and the needed time to obtain the data. If measurements are taken during the continuous heating from a low temperature as is often done, the data will be perturbed somewhat by the effects discussed here.

References and Notes

(1) Kovacs, A. J. *J. Polym. Sci., Part C* **1958**, *30*, 131.
(2) Kovacs, A. J. *Adv. Polym. Sci.* **1963**, *3*, 394.
(3) Kovacs, A. J.; Stratton, R. A.; Ferry, J. D. *J. Phys. Chem.* **1963**, *67*, 152.
(4) Struik, L. C. E. *Physical Aging in Amorphous Polymers and Other Materials*; Elsevier: Amsterdam, 1978.
(5) Struik, L. C. E. *Polym. Eng. Sci.* **1977**, *17*, 165.
(6) Smith, T. L.; Levita, G.; Moonan, W. K. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 875.
(7) Kovacs, A. J. In Structure and Mobility in Molecular and Atomic Glasses. O'Reilly, J. M.; Goldstein, M., Eds.; *Ann. N.Y. Acad. Sci.* **1981**, *371*, 38-64.
(8) Struik, L. C. E. *Polymer* **1988**, *29*, 1347.
(9) Haidar, B.; Smith, T. L. *Polymer*, in press.
(10) Illers, K. H.; Breuer, H. *Kolloid-Z.* **1961**, *176*, 110.
(11) Ricco, T.; Smith, T. L. *J. Polym. Sci., Polym. Phys. Ed.* **1990**, *28*, 513.
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Low-Temperature Crystal-Crystal Phase Transitions in Triblock Semifluorinated *n*-Alkanes

Temperature-induced phase transitions have been observed and characterized in *n*-alkanes,[1] perfluoro-*n*-alkanes,[2] and a number of long-chain polymers.[3-5] In a limited number of cases, phase transitions have also been observed when these materials are subjected to high pressure.[6,7] In general, phase transitions may be classified into at least two groups: order-disorder and crystal-crystal transitions. In the former, the lattice structure is preserved, but the conformational order of the chain is altered at the phase transition. On the other hand, at crystal-crystal transitions lattice structural changes occur, but conformational order is preserved although it may change from one ordered form to another. In many cases a crystal-crystal transition gives rise to a different symmetry of the unit cell, which, in turn, manifests itself as a change in the spectroscopic selection rules.

Recently, a series of semifluorinated diblock,[8-11] $F(CF_2)_n(CH_2)_mH$ [FnHm], and triblock,[12] $F(CF_2)_n(CH_2)_m(CF_2)_nF$ [FnHmFn], copolymers have been synthesized and characterized in the solid state and in the melt. In the FnHm diblocks,[9] a high-temperature crystal-crystal phase transition was observed, which was very similar to the "rotator" phase found for many *n*-alkanes. No such transition was observed for their triblock FnHmFn analogues. The purpose of this paper is, however, to report the first observation of a low-temperature phase transition in a triblock compound during which a rearrangement of the chains within the unit cell occurs.

The triblock semifluorinated *n*-alkane, F12H10F12, used in this study was synthesized from perfluorododecyl iodide and 1,9-decadiene in a procedure analogous to that utilized for the preparation of other F12HmF12 compounds.[12] A detailed description of the instrumentation used for the variable-temperature measurements contained in this work has been given previously.[8]

As shown in Figure 1, the room-temperature Raman spectra of F12H10F12 can be understood as a simple composite spectrum originating from a superposition of a fluorocarbon and a hydrocarbon spectrum. The sharp bands between 1000 and 1500 cm^{-1} shown in Figure 1 are characteristic of vibrational motions of the $-CH_2-$ hydrocarbon segment with the exception of the narrow symmetric $-CF_2-$ stretching band at 1380 cm^{-1} and the broad feature at 1215 cm^{-1} attributable to CC stretching and CCC bending.[13,14] As can be seen in Figure 1, the spectra at 60 and 14 °C are identical since no high-temperature phase transition, like that which occurs in certain of the diblock FnHm molecules,[9] exists in the triblock F12H10F12. However, in this case a substantial change in the Raman spectrum is observed instead at subambient temperatures. A phase transition occurs below 14 °C (a weak DSC transition is observed at 14-18 °C upon cooling at 10 °C/min) and is manifested by a change in relative intensity of the CC stretching bands in the 1050-1150-cm^{-1} region and the appearance of a sharp band in the $-CH_2-$ bending region at 1415 cm^{-1}. The latter feature

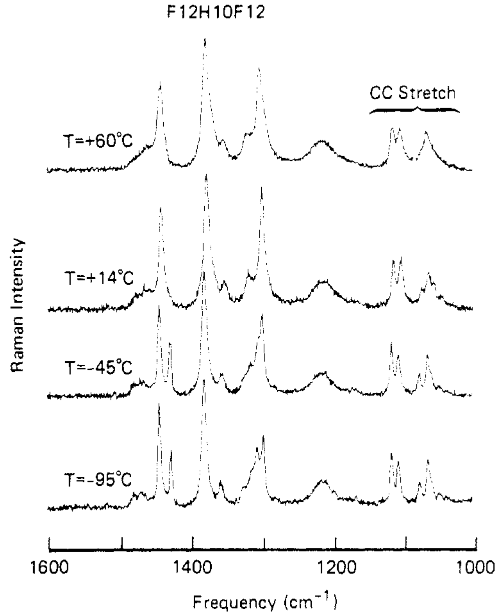

Figure 1. Raman spectra of F12H10F12 obtained as a function of temperature. Data were obtained at 2-cm^{-1} resolution using 200 mW of laser power at 488.0 nm.

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