Variable-Temperature ^{13}C NMR Studies of Carbonyl Motion in Solid Bisphenol-A Polycarbonate

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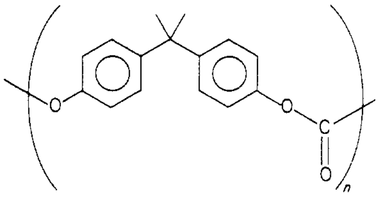
ABSTRACT: Variable-temperature ^{13}C NMR spectra of bisphenol-A polycarbonate, isotopically labeled with ^{13}C at the carbonyl position, have been analyzed in terms of local motion of the carbonate group. Slight variation of the observed powder pattern occurred as the temperature was varied from −255 °C to room temperature. Nevertheless, a computer analysis showed that oscillation about the chain axis through a total angle of 40° is consistent with the results.

Introduction

Because bisphenol-A polycarbonate (BPAPC) has an unusually high impact strength, there has been a great deal of interest in the elucidation of its dynamic properties. Nuclear magnetic resonance is one of a number of tools that have been used for this purpose.[1]



bisphenol-A polycarbonate

There are various ways in which NMR may be used for the study of motion in solid polymers. One approach involves the analysis of ^{1}H NMR line shapes and relaxation parameters. The proton line shapes of most solid polymers are difficult to interpret, however, because of the presence of many different coupled protons in the solid sample. For the same reason it is difficult to isolate the relaxation behavior of individual protons of interest. Despite these limitations, ^{1}H NMR spectroscopy has given valuable information about motions in polycarbonates but has not revealed the details of how the motions occur.[2]

Recent attention has been focused on the ^{13}C NMR spectra of solid polymers. The combined application of high-powered decoupling of protons from the ^{13}C nuclei and magic-angle spinning allows the resolution of carbon signals from many different sites in many polymers, including BPAPC.[3] Nuclear relaxation parameters for carbon, such as the time constants for relaxation in either the laboratory or the rotating frames, may be measured selectively, allowing the researcher to specify which molecular sites are involved in a given motion.

Still, problems remain in the use of ^{13}C relaxation times for the study of polymer mobility. Carbon nuclear relaxation in the rotating frame can occur by mechanisms unrelated to polymer motion, for example.[4]

Even when the relaxation has been determined to be motional in origin, as apparently is the case for BPAPC,[3d] the relaxation parameters provide limited data on which to base conclusions about the mechanisms of internal motion. To be most useful, for example, the relaxation measurements should be made at many different temperatures, and few laboratories are currently equipped to do magic-angle spinning at variable temperatures.

Deuterium NMR provides another powerful way to study motion in solid polymers.[5] The most useful feature of the deuterium spectrum is once again the line shape. Because the deuterium line shape is determined almost entirely by the quadrupole interaction, the theoretical analysis is much more straightforward than it was for the proton spectrum. Of course, labeled compounds must be used, but synthesis of compounds with deuterium in specific chemical sites is often straightforward and inexpensive. Variable-temperature experiments are simple because magic-angle spinning is not needed.

Deuterium NMR has been used to study polycarbonates containing deuterium on the aromatic ring and in the methyl groups[5,6] but cannot be used directly for a study of carbonyl motion. A complete picture of motion in the polycarbonate system should include a description of the behavior of the carbonyl site, however. Recent calculations indicate that the phenyl rings and the carbonyl unit must necessarily reorient in a cooperative fashion.[2j] Furthermore, at least part of the low-temperature transition detected with mechanical and dielectric measurements is associated with a combined phenyl ring and carbonyl motion.[1] The motions responsible for the high impact strength of polycarbonate are likely to be cooperative,[7] involving several different monomer units linked by the carbonyl groups.

The line shapes of ^{13}C spectra taken without magic-angle spinning provide another source of information about polymer motion. The shapes are largely determined by the anisotropic chemical shift, whose angular dependence is again well understood. Typical ^{13}C chemical shift anisotropies are about 2 orders of magnitude smaller than the quadrupole coupling constants for most deuteriums in organic compounds. This means, as we will explain later, that the chemical shift powder pattern is sensitive to much slower motions than is the deuterium powder pattern. Dipolar coupling interactions, which are difficult to include in the analysis when there are many different nuclei coupled together, do not complicate the interpretation because the dipolar interaction between two carbons is not nearly so strong as that between two protons, and even in an enriched sample the density of ^{13}C nuclei is much less than that of protons.

A complication in the use of powder patterns from the ^{13}C chemical shift anisotropy is that the overlapping signals from the many different carbons in most compounds may make analysis impossible. A solution is to work with labeled materials, in which the signal from a single important carbon is so enhanced relative to the rest of the spectrum that it can effectively be treated individually. The potential problem of dipolar interactions among the labeled carbons resulting in undesirable spectral broadenings is avoided if the labeled carbons constitute a small fraction of the total sample.

We report here our studies on bisphenol-A polycarbonate labeled with ^{13}C at the carbonyl group. Our work parallels research done elsewhere with polycarbonate

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labeled in the aromatic ring.[8]

Experimental Section

The ^{13}C-labeled bisphenol-A polycarbonate was synthesized from labeled phosgene (Merck, 90% ^{13}C, in benzene, used as received). To a solution of 2.7 g (0.012 mol) of bisphenol-A in 10 mL of methylene chloride and 2.2 mL of pyridine was added 1.3 g (0.013 mol) of ^{13}C-labeled phosgene in benzene. The addition required 20 min. The reaction was stirred for 30 min more and then acidified with dilute HCl. The phases were separated, and the organic phase was washed three times with water. The polymer was collected by precipitation into excess methanol. Drying under vacuum at 60 °C gave 1.8 g of polymer.

High-resolution ^{13}C NMR (in solution) of the polycarbonate confirmed enrichment to greater than 90% at the carbonyl position. The polymer was characterized by gel permeation chromatography (GPC), dilute solution viscometry, and thermal analysis. From $[\eta] = 0.215$ in methylene chloride at 25 °C, M_w was estimated to be 8900 ± 600 according to the data of Berry et al.[9] From $T_0 = 127$ °C at a heating rate of 20 °C/min, and from the data of Merrill and Petrie,[10] M_n was estimated at 3300 ± 200; thus, $M_w/M_n = 2.7 \pm 0.3$.

Samples from which the NMR spectra were obtained were prepared by molding at 235 °C under 5000 lb/in.^{2} pressure and quenching in ice at atmospheric pressure. As an example of polycarbonate with ^{13}C in natural abundance, a commercial sample of Lexan 145 (General Electric Co.) was prepared in the same way.

Most of the ^{13}C NMR spectra were acquired at 25.18 MHz on a Bruker CXP-100 spectrometer. For a typical experiment, 90° pulses for either ^{1}H or ^{13}C were 5 μs long. Spectra were generated with cross polarization times of 1–4 ms. The measured time for probe ringing to die away after a pulse was 30 μs. Spectral accumulation was thus delayed by 25 μs (one dwell time) following cross polarization to minimize artifacts. Spin–temperature alternation in the rotating frame was then used to cancel most of the residual signal from the probe.[11] A delay of exactly one dwell time does not lead to distorted line shapes[12] because the initial point in the time domain merely establishes the mathematical base line in the frequency domain.

Slight curvature in the base line persisted in spite of the precautions described in the previous paragraph. This was removed artificially with the base-line-correction procedure available in the Bruker software. Comparison of the spectra before and after the correction showed that the basic line shape was not changed. Removal of base line roll greatly facilitated comparison of experimental and calculated spectra.

Free-induction decays were recorded and stored in 1K of computer memory. Exponential multiplication equivalent to 100-Hz spectral broadening was applied prior to Fourier transformation. Temperature on the Bruker CXP-100 spectrometer was controlled with the standard equipment supplied by the manufacturer. The measured temperature was accurate within 1 °C, by comparison with the temperature of a thermocouple inserted into a dummy sample when the probe was cooled on a bench top. The largest actual error in temperature was ±2 °C.

Chemical shifts in the spectra recorded at 25.18 MHz were measured relative to a sealed capillary of tetramethylsilane inserted into the sample. Even below its freezing point Me_4Si gives a relatively sharp signal whose frequency is essentially the same as that of the liquid. The frequencies measured directly from the spectrometer changed with temperature, presumably because at the lowest temperatures the high flow rates of cold nitrogen cooled the probe and the inside of the magnet assembly.

Spectra acquired at 50 MHz were recorded on a home-built system based on an Oxford cryomagnet.[13] The variable-temperature probe for this system was constructed by Chemagnetics (Fort Collins, CO) for 10-mm samples. The data system was a Nicolet 1180 computer with a Nicolet 293B pulse programmer. Spectra were obtained at 15 MHz on a home-built spectrometer at the University of Utah and at 75 MHz on a Bruker CXP-300 spectrometer at the National Research Council in Ottawa, Ontario.

The nuclear Overhauser enhancement of the carbonyl signal was measured at 50 MHz by a gated technique in which the enhanced spectrum was recorded following a long pulse train with a duty cycle of 12% applied to the proton during a relaxation delay of 75 s. Spectra without enhancement were accumulated with high-power decoupling after a 90° pulse. The spin–lattice relaxation time of the carbonyl carbon was 10 s.

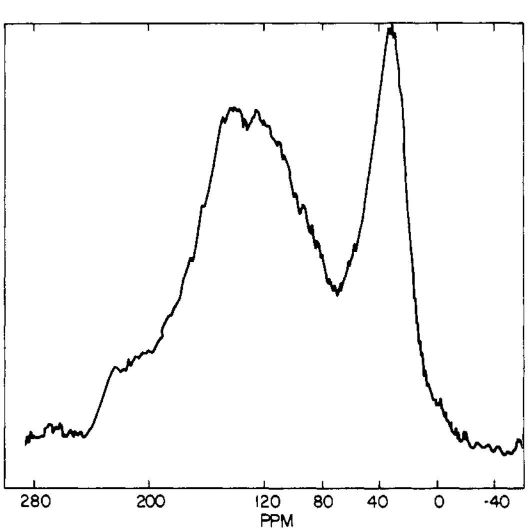

Figure 1. Natural-abundance ^{13}C NMR spectrum without magic-angle spinning of bisphenol-A polycarbonate at room temperature and a frequency of 25 MHz. The spectrum is an average of 514 scans and has been artificially broadened by 100 Hz.

Results

Figure 1 shows the spectrum at 25 MHz of bisphenol-A polycarbonate with ^{13}C in natural abundance. It is essentially the same as one published by Schaefer, Stejskal, and Buchdahl.[3a] The sharpest feature is the methyl signal at about 35 ppm. A portion of the carbonyl resonance is just visible at the left-hand edge of the spectrum. Lowering the temperature to −123 °C noticeably broadened the spectrum, but it was difficult to identify specific changes in the spectral features. The methyl signal did decrease in relative intensity at low temperatures, presumably because cross polarization or decoupling becomes ineffective.[14]

Figure 2 contains the ^{13}C spectrum of the labeled polycarbonate at 25 MHz and 12 °C. Most of the spectrum comes from the carbonyl group. The much smaller signal to its right is from the methyl carbons and the carbon to which they are attached. Even in natural abundance these atoms give a significant signal because there are three of them and the pattern is relatively narrow.

The pattern for the carbonyl carbon at −177 °C is only slightly different from that in the room-temperature spectrum (see Figure 3). With decreasing temperature there is a slow expansion in the band with a gradual increase in the prominence of the shoulder on the right-hand edge. Thus the shoulder on the right-hand side of the spectrum is slightly more obvious at −177 °C than it is at room temperature. No substantial changes in the pattern occurred when the temperature was lowered from −96 (177 K) to −255 °C (18 K) on the spectrometer at the University of Utah operating at 15 MHz. Spectra run at temperatures as high as 100 °C are essentially the same as those acquired at room temperature.

The enhancement of the shoulder with decreasing temperature was more noticeable for spectra taken at frequencies of 50 or 75 MHz than for those taken at 25 MHz, but the overall results are equivalent to those obtained at 25 MHz. There is again no narrow temperature range over which the enhanced shoulder suddenly appears.

The spectrum taken at −177 °C was fit closely by a theoretical spectrum calculated with principal values of the chemical shift of 234.2, 123.0, and 84.1 ppm. The

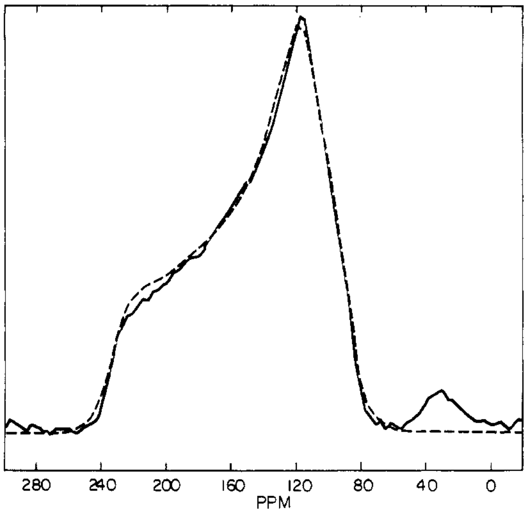

Figure 2. ^{13}C NMR spectrum without magic-angle spinning of amorphous bisphenol-A polycarbonate labeled with ^{13}C at the carbonyl carbon. The spectrometer frequency was 25 MHz, and the temperature was 12 °C. Exponential weighting of the time-domain function equivalent to 30 Hz line broadening was used. The dotted line shows the theoretical spectrum calculated for principal elements of the chemical shift tensor at 234.2, 123.0, and 84.1 ppm with oscillation of the carbonyl group through an angle of 40° about an axis perpendicular to the carbonyl group and through 15° about an axis parallel to the carbonyl group (see text).

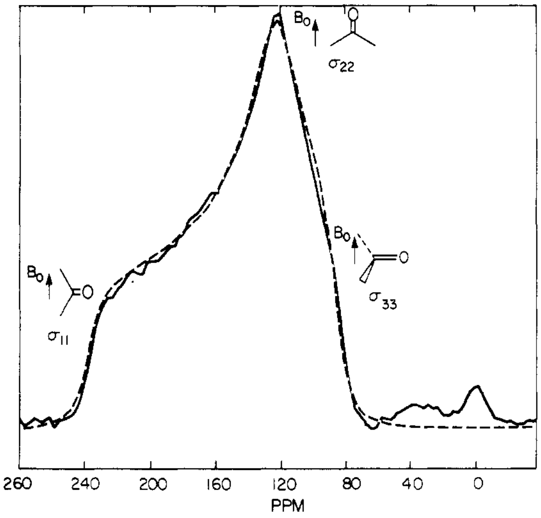

Figure 3. ^{13}C NMR spectrum of amorphous bisphenol-A polycarbonate, labeled with ^{13}C at the carbonyl carbon, at 25 MHz and −177 °C. The dotted line shows a simulated spectrum calculated with the chemical shift elements shown in Figure 2 and no motion.

theoretical spectrum was broadened artificially with a Gaussian function and 200 Hz of Lorentzian broadening.

In an attempt to enhance the effect of motion on the NMR results, we have also done a series of spin-echo experiments. The spin-echo experiment effectively measures the line widths of the individual components of the inhomogeneously broadened chemical shift anisotropy pattern.[15] Motional averaging may have a more pronounced effect on the widths of these single components than it does on the overall powder pattern.

Spin echoes were created with 180° pulses in a series of experiments in which the interval between the cross-polarization period and the 180° pulses was systematically varied. Free-induction signals starting at the tops of the echoes were then Fourier transformed to give spectra from which the rate of decay of intensity at various points in the powder pattern could be determined. The actual shape of the pattern changed only slightly as the delay period was varied. The overall decay rate was almost independent of temperature.

Spectra acquired with nuclear Overhauser enhancement were 1.6–2.1 times more intense than spectra acquired without enhancement. The increase may have been slightly greater for the high-frequency than for the low-frequency edge of the spectrum, but the difference is within the experimental error of the measurement.

Discussion

The anisotropic chemical shift offers a useful probe of the orientation of molecules in the solid phase. The shape of the observed band of frequencies in the NMR spectrum can be used to measure the distribution of orientation frequencies of the molecules, for example.[16] A computer can simulate the shape of the NMR band from the orientational distribution function, usually by numerical methods, if the chemical shift tensor is known.

The band shapes are most easily related to orientation when the chemical shift tensor is axially symmetric. In this case there is a one-to-one relation between the frequencies in the NMR spectrum and orientation of the axially symmetric molecule. In the general case, nuclei in molecules of several different orientations may absorb at the same NMR frequency, but even then there are procedures for the extraction of the orientation information.[16]

Our interest is not in the static but in the dynamic molecular orientation, however. Changes in the molecular orientation occurring at a rate comparable to the time scale defined by the range of frequencies in the spectrum lead to characteristic changes in the NMR band shapes that can be used to give information not only about the rates of the reorientation but also about details of the geometry of the motions.[17,18]

The changes in the NMR patterns as a result of motion are closely related to the averaging effects caused by interchanges of chemically different nuclei in the NMR spectra of liquids.[19] The difference in the solid is that there is a continuous range of chemical shifts that are affected by the motional process rather than discrete frequencies.[20]

We can now use what is known about dynamic NMR of liquids[19] to predict qualitatively how carbonyl motion will affect the NMR spectrum of bisphenol-A polycarbonate. Maximum spectral broadening occurs for liquids when two resonances of equal intensity are averaged at a rate comparable to the frequency separation of the signals. In solids we expect that the effective NMR time scale will be determined by the total range of frequencies affected by the motional process. The width of the chemical shift pattern sets an upper limit for this range, although for most processes any given orientation cannot be converted into all other orientations on the NMR time scale, and the effective range will be reduced. The actual spread of frequencies that are averaged will be determined by the geometry and amplitude of the motion involved.

Because the spectral band for the carbonyl in the polycarbonate expands only slightly with decreasing temperature, we know that spectral components of widely different frequencies cannot be averaged by chain reorientation. We will estimate that the averaging occurs over ranges of only about 100 Hz. For a frequency of 100 Hz the maximum loss in the dielectric relaxation spectrum comes at about −90 °C.[1,2i,l] Thus we estimate that reorientational processes will probably produce minimal spectral averaging in spectra acquired at temperatures significantly below −90 °C. If we have underestimated the effective averaging range, the transition temperature will be somewhat higher than −90 °C, but the loss peak in the dielectric spectrum is extremely broad, and we should not be able to define a transition temperature very accurately in any case.

The assumption of spectral averaging of only a narrow range of frequencies by the motional process is consistent with the rather long nuclear Overhauser enhancement observed at room temperature. Motions occurring fast enough to produce extensive spectral averaging at 18 K would be fast enough at room temperature to contribute to spin–lattice relaxation through the chemical shift anisotropy mechanism. The large nuclear Overhauser enhancement indicates that spin–lattice relaxation of the carbonyl carbon is largely dipolar, however. In solids the maximum NOE will probably not occur even for purely dipolar relaxation because the conditions for extreme narrowing are not met.[22]

It is, of course, conceivable that the carbonyl group is not involved in any reorientations of significant amplitude at all. This conclusion would provide a simple explanation of the minimal changes in the NMR spectrum with temperature variations, but dielectric relaxation results clearly indicate a low-temperature loss. In polycarbonate it is difficult to explain the dielectric behavior in terms of motion that does not involve the dipolar carbonyl group. Furthermore, a completely rigid carbonyl group implies that the aromatic portions of the chain reorient almost independently of each other. Cooperative motion of the aromatic rings and the carbonyl group has been predicted theoretically[2k] and has been invoked to explain at least part of the low-temperature mobility in polycarbonate seen by dielectric and mechanical relaxation.[1]

Careful analysis of the variable-temperature spectra by computer simulation shows, in fact, that a surprisingly large amount of carbonyl motion is consistent with the observations. Perhaps more important, certain modes of carbonyl reorientation can be ruled out by the NMR results.

We must start with an assignment of the principal values of the chemical shift tensor to particular orientations of the carbonyl group. Ideally this is done with analysis of the rotation behavior of the spectrum of a single crystal. In the absence of such a crystal, we have made assignments based on information from other compounds.[23]

Spiess shows that, except for calcium carbonate, the most shielded component of the chemical shift tensor of the carbonyl group generally has a value between 80 and 115 ppm when the reference compound is tetramethylsilane.[23b] This component is directed perpendicular to the sp^2 plane in all compounds that have been checked.

The least-shielded component for other carbonyl compounds has values between 235 and 280 ppm. This component lies in the sp^2 plane perpendicular to the CO bond. The third component has values between 115 and 235 ppm and is parallel to the CO bond. Our shifts lie within the ranges compiled by Spiess, and we assume that the orientations he proposes are reasonable for the polycarbonate. An error in the assignments would change the axes about which orientational motion can occur and still be consistent with the experimental results. The overall analysis would be the same. The assignments are indicated in Figure 3.

We have chosen to simulate the motion of the carbonyl group in terms of a jump of the carbonyl between two sites of equal energy separated by an energy barrier. The assumption of an activated reorientation process is consistent with the temperature dependence of the dielectric relaxation spectrum but may also be used as a first approximation of the effects of libration within a potential well. In a very simple case the carbonyl rotates around an axis perpendicular to the C=O bond in the plane formed by the three oxygen atoms. This corresponds to partial averaging of the tensor elements σ_{22} and σ_{33}. We assume that at room temperature reorientation is very fast on the effective NMR time scale. Reasonably good fits of the experimental results can be obtained when the angle between the two sites is 40°.

Motion of the type described in the previous paragraph is not unreasonable in that the axis of rotation lies parallel to the long axis of the polymer chain. Motion in the real system is probably more complicated, however, so we have also made calculations with a slightly modified model. Superimposed on the rotation along the axis described above we have incorporated rotation about an axis along the C=O bond. Simple experiments with molecular models suggest that such a model is reasonable, and, indeed, it leads to a better fit of the room-temperature results with an angle of rotation of 40° about the long axis and 15° about the C=O bond (see Figure 3). This type of motion would necessarily require that carbonate motion be coupled with that of the aromatic rings.

Most of our computer matching was made with spectra acquired at 25 MHz. The same chemical shift parameters and motional models also led to satisfactory fits of the spectra taken at 75 MHz, however.

Measurement of the chemical shifts of the powder patterns with greater precision on an absolute basis might help in further discrimination among different motional models. For example, a process which averages σ_{11} and σ_{22} does not change the high-frequency end of the spectrum. Our method of referencing chemical shifts directly to the signal of tetramethylsilane still does not allow us to pinpoint with confidence the spectral regions most affected by the motional process. A more precise method of measuring chemical shifts in the solid at low temperature would be difficult to devise, however. If the spectral effects were more pronounced, referencing would not be so critical.

Because the observed changes in the NMR spectrum with temperature are slight, we have not attempted to test more complex motional models. It is obvious that as the number of flexible features in the model increases, the ability to fit almost any experimental result improves. The significance of the results is that certain models are completely incompatible with the experimental results. For example, motions resulting in large-scale averaging of tensor elements σ_{11} and either σ_{22} or σ_{33} are not satisfactory.

The slight effects of temperature on the NMR spectrum also do not justify an attempt to match the line shapes at various temperatures by variation of the rate of the motional process. Such matching would be complicated in any case by the distribution of activation energies associated with motion in polymers.

The results of Spiess[5,6] and Inglefield and co-workers[8] on the motion of the aromatic rings are consistent with our results. Both ^{13}C NMR and deuterium NMR indicate that the primary motion of the phenyl rings involves 180° flips. This type of motion is probably rather local and, as such, may not couple to motion of the carbonyl group. Spiess, however, found that on top of the ring flipping the aromatic rings undergo an oscillatory motion. The total angle of oscillation is 30° at room temperature but increases to 70° at 380 K. Although the effective axis about which oscillation occurs is different for the two groups, the amplitudes for the aromatic rings and the carbonyl groups appear to be approximately the same. It is tempting to assume that this type of motion does couple with that of the carbonyl group. While we will not allow ourselves to succumb to this temptation, we do observe that such cooperative effects have been postulated.[1,2a,21,24] Calculations of the energy barriers for conformational processes involving both the aromatic rings and the carbonyl group might be helpful in clarifying whether cooperative processes are indeed possible.[2k]

We have assumed that the reorientation of the carbonyl group occurs as an activated process involving passage over an energy barrier. The presence of the barrier makes the rate of the process temperature dependent and accounts for the temperature-dependent dielectric relaxation loss. Calculations have shown that in the most favorable conformation of polycarbonate the aromatic rings are perpendicular to the plane of the carbonyl group.[25] A clear source of a barrier from intramolecular considerations alone is not easy to see. This may mean that the barrier derives from intermolecular packing effects on the individual polymer chains. Such packing effects may very well also be the source of the wide range of distribution frequencies found for polycarbonates and other polymers.[26,27] Motion in a potential well with only the amplitude being temperature dependent cannot be ruled out by the NMR results, however.

Conclusion

Although the NMR spectral changes with temperature were not as dramatic as we had hoped they might be, they still have shown that the carbonyl group can undergo rotational motion through an angle of as much as 40°. The results provide useful limits on the motion the carbonyl group undergoes during the motion of the polycarbonate chain as a whole.

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Registry No. ((Bisphenol A)·phosgene) (copolymer), 25971-63-5; bisphenol A polycarbonate (SRU), 24936-68-3.

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