Local Motions between Unequivalent Conformations in Solid Poly(cyclohexyl methacrylate): A Variable-Temperature Magic-Angle Carbon-13 Nuclear Magnetic Resonance Study

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ABSTRACT: Variable-temperature high-resolution solid-state ^{13}C NMR experiments have pointed out the existence of side-ring motions with correlation times of the order of 10^{-6} s in solid poly(cyclohexyl methacrylate). The line broadening resulting from motional modulation of the carbon-proton dipolar coupling has been analyzed in terms of a chair-chair inversion of the side-ring between unequivalent conformations. Characteristics of this motion as a function of temperature have been determined. Results thus obtained are in good agreement with conclusions derived by Heijboer from mechanical measurements on the same polymer and use of conformational energy calculations.

Cross-polarization (CP) magic-angle spinning (MAS) dipolar decoupled (DD) ^{13}C NMR has proved to be a powerful tool for demonstrating the existence of molecular motions in the solid state. In a previous study,[1] room-temperature spectra together with measurements of carbon-13 spin-lattice relaxation times in the rotating frame pointed out the presence of rapid ring motions, with correlation times of the order of 10^{-6} s, in poly(cyclohexyl methacrylate). However, in order to carry out a more precise characterization of these ring processes, variable-temperature experiments are necessary. Such variable-temperature experiments are reported in the present paper.

Experimental Section

Carbon-13 NMR experiments were performed at 12.07 MHz with a home-built spectrometer constructed around a 12-in. Varian electromagnet and employing external ^2H field frequency stabilization, solid-state class-A transmitters, and a double-tuned single-coil probe.[2]

Spectra were obtained as a function of temperature using magic-angle spinning in a hollow cylindrical rotor made of Macor and spinning speed ranging from 1.5 to 2 kHz.[3] The inner spinner volume was approximately 0.5 cm^3. All the spectra were obtained by cross polarization from the spin-locked protons followed by high-power proton decoupling.

Matched spin-lock cross-polarization transfers employed a radio-frequency (rf) field strength (H_1) of 32 kHz. Spectra were recorded under the condition of optimum single contact, which was found to be 1-2 ms. In all the spectra, spin temperature-inversion techniques were employed to minimize base-line noise and roll.[4] Flip-back[5] was also systematically used to shorten the delay time between two successive pulse sequences. A total of 2000-4000 scans was needed to obtain a good signal-to-noise ratio.

Poly(cyclohexyl methacrylate) (Aldrich, 194-9) is commercially available.

Line-Broadening Mechanisms

Line-broadening mechanisms in glassy materials have been recently reviewed.[6] Some of them, the static ones (bulk susceptibility of the sample, chemical shift dispersions due to packing effects, bond distortion, and conformational inequivalence), induce only a small effect. More important may be the line broadenings arising from relaxation processes such as motional modulation of the chemical shift anisotropy[7] and motional modulation of the dipolar carbon-proton coupling.[8] For an aliphatic carbon in a static magnetic field of 1.4 T, the broadening due to the motional modulation of the chemical shift anisotropy can be estimated to remain less than 7 Hz.[6] Therefore, in the case of an aliphatic carbon in a low static field and under suitable conditions of magic-angle setting and proton-decoupling irradiation the only important cause of motional broadening comes from modulation of the dipolar C-H coupling. This mechanism is maximum when the rate of molecular motion is equal to the proton-decoupling field strength in frequency units: $\omega_{1H} = \gamma_H H_{1H}$. For slow motions, this broadening is much larger than that due to the previous static effects. Therefore the observed full line width at midheight may be written as

$$\Delta = (\pi T_{2m})^{-1} + (\pi T_{2res})^{-1} = (\pi T_{2T})^{-1} \qquad (1)$$

where the residual line width $(\pi T_{2res})^{-1}$ accounts for the various static effects.

Under the conditions that proton irradiation is applied exactly on resonance, that the sample spinning rate is much smaller than ω_{1H}, and that the motion does not change the carbon-proton distance, which means that we consider only the single-bond interactions, the transverse relaxation time T_{2m}, resulting from this mechanism and contributing an amount $(\pi T_{2m})^{-1}$ to the line width, is[8]

$$(T_{2m})^{-1} = A_{CH} J(\omega_{1H}) \qquad (2)$$

A_{CH} is the square of the carbon-proton dipolar coupling strength. For one proton at a distance r from the carbon under interest

$$A_{CH} = \gamma_H^2 \gamma_C^2 \hbar^2 / r^6 \qquad (3)$$

$J(\omega)$ is the spectral density of the fluctuations of the dipolar interaction

$$J(\omega) = \int_{-\infty}^{+\infty} G(\tau) e^{-i\omega\tau} \, d\tau \qquad (4)$$

where $G(\tau)$ is the autocorrelation function

$$G(\tau) = F(t) F^*(t + \tau) \qquad (5)$$

with

$$F(t) = (1 - 3 \cos^2 \beta(t))/2 \qquad (6)$$

where β is the angle of the vector C-H r of interest with

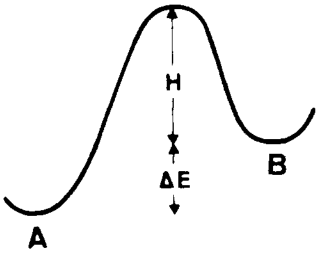

Figure 1. Two-potential-well model for the cyclohexyl ring inversion.

the static magnetic field direction.

The simplest form of the powder average of $G(\tau)$ is

$$G(\tau) = (K/5)\exp(-\tau/\tau_c) \tag{7}$$

so that

$$J(\omega) = \frac{K}{5}\frac{\tau_c}{1 + \omega^2\tau_c^2} \tag{8}$$

where K ($K \leqslant 1$) describes how much the carbon–proton dipolar interaction in a powder is modulated by the motion.

For a methylene carbon in a rf field $\omega_{1H} = 2\pi \times 32$ kHz, even if only a tenth of the rigid-lattice second moment is modulated by the motion, the motional broadening for a 12-MHz ^{13}C observation is larger than the static one, which does not exceed 6 ppm, for motions whose correlation times are in the range 10^{-4}–2×10^{-7} s, which can therefore be studied from the line broadening.

The model considered now is a two-state system with equilibrium positions A and B whose energies are E_A and E_B. H and $H + \Delta E$ are the energy barriers separating states B and A and states A and B, respectively (Figure 1). We assume a Boltzmann statistics and suppose that the flips from A to B and from B to A constitute a stationary process with rates $W_{A\rightarrow B}$ and $W_{B\rightarrow A}$

$$W_{A\rightarrow B} = \tau_0^{-1}\exp[-((\Delta E + H)/RT)] = (\tau_0 ab)^{-1} \tag{9}$$

$$W_{B\rightarrow A} = \tau_0^{-1}\exp[-(H/RT)] = (\tau_0 b)^{-1} \tag{10}$$

where $\Delta E = E_B - E_A$, $b = \exp(H/RT)$, and a is the ratio of the equilibrium populations

$$a = p(\mathrm{A})/p(\mathrm{B}) = \exp(\Delta E/RT) \tag{11}$$

Let the correlation time τ_c be defined as

$$\tau_c^{-1} = W_{A\rightarrow B} + W_{B\rightarrow A} = \tau_0^{-1}(1 + a)/ab \tag{12}$$

Look and Lowe have calculated the autocorrelation function associated with such a model. It can be written as[9]

$$G(\tau) = F(t)F^*(t + \tau) = \frac{(aF_A + F_B)^2 + a(F_A - F_B)^2\exp(-\tau/\tau_c)}{(1 + a)^2} \tag{13}$$

In our case F_A and F_B are the spherical harmonics defined by formula 6 and associated to equilibrium positions A and B.

A simple way to compute $G(\tau)$ is to use the spherical harmonic addition theorem together with the orthogonality relation of the Wigner rotation matrices on the unit sphere:[10] It is easily shown that the powder average of a product of two spherical harmonics depends only of the angle θ between the two directions (β_1, γ_1) and (β_2, γ_2)[10]

$$\langle Y_2^0(\beta_1,\gamma_1)Y_2^0(\beta_2,\gamma_2)\rangle_{\text{powder}} = \frac{P_2(\cos\theta)}{4\pi} \tag{14}$$

where the brackets indicate the powder average. As

$$F(\beta) = (4\pi/5)^{1/2}Y_2^0(\beta,0) \tag{15}$$

one gets

$$\langle F(\beta_1)F(\beta_2)\rangle_{\text{powder}} = P_2(\cos\theta)/5 \tag{16}$$

and

$$\langle F_A^2\rangle_{\text{powder}} = \langle F_B^2\rangle_{\text{powder}} = 1/5 \tag{17}$$

$$\langle F_AF_B\rangle_{\text{powder}} = (3\cos^2\theta - 1)/10 = x/5$$

with $x = P_2(\cos\theta)$.

Thus, using the expression of $G(\tau)$ given by formula 13

$$G(\tau) = \frac{(a^2 + 2ax + 1) + 2a(1 - x)\exp(-\tau/\tau_c)}{5(1 + a)^2} \tag{18}$$

Terms that are independent of τ do not induce motional line broadening. The other terms give

$$J(\omega) = \frac{4a}{(1 + a)^2}\frac{1 - x}{10}\frac{\tau_c}{1 + \omega^2\tau_c^2} \tag{19}$$

When the two states A and B present equal energies ($\Delta E = 0$), $a = 1$ and

$$J(\omega) = \frac{1 - x}{10}\frac{\tau_c}{1 + \omega^2\tau_c^2} \tag{20}$$

with $\tau_c = (\tau_0\exp(H/RT)/2$.

For a CH$_2$ carbon in the particular case of $\theta = 109°28'$, $x = -^1/_3$, and the minimum value of T_{2m} is 6.3×10^{-5} s for an irradiation frequency of 32 kHz, assuming a value of r of 1.07 Å.

In the general case where a is different from 1, that is, E_A is different from E_B, $(T_{2m})^{-1}$ is lengthened and can be written for a CH$_2$ group as

$$(T_{2m})^{-1} = 2A_{CH}J(\omega_{1H}) = 2A_{CH}\frac{4a}{(1 + a)^2}\frac{1 - x}{10}\frac{\tau_c}{1 + \omega_{1H}^2\tau_c^2} \tag{21}$$

If a is much greater than 1, τ_c^{-1} may be simplified as

$$\tau_c^{-1} = \tau_0^{-1}\exp(-H/RT) = (b\tau_0)^{-1} \tag{22}$$

In the case of fast flips of the internuclear vector from position B to A ($\omega_{1H}^2\tau_c^2 \ll 1$), $J(\omega_{1H})$ adopts the following simplified expression:

$$J(\omega_{1H}) = \frac{4a}{(1 + a)^2}\frac{1 - x}{10}\tau_c = \frac{4(1 - x)}{10}\frac{\tau_0\, b}{a} \tag{23}$$

On the contrary, for slow motions ($\omega_{1H}^2\,\tau_c^2 \gg 1$)

$$J(\omega_{1H}) = \frac{4(1 - x)}{10}\frac{1}{\tau_0 ab\omega_{1H}^2} \tag{24}$$

Therefore, at temperatures above the minimum

$$T_{2m} \propto \exp((\Delta E - H)/RT) \tag{25}$$

whereas at temperatures below the minimum

$$T_{2m} \propto \exp((\Delta E + H)/RT) \tag{26}$$

Generally, the T_{2m} minimum is observed for

$$\omega_{1H}^2\tau_c^2 = \frac{H(1 + a) + \Delta E(2 - a)}{H(1 + a) + a\Delta E} \tag{27}$$

Under the assumption that a is much greater than 1, the minimum of T_{2m} is observed for

$$\omega_{1H}^2\tau_c^2 = (H - \Delta E)/(H + \Delta E) \tag{28}$$

which corresponds to

$$(T_{2m}^{-1})_{\text{minimum}} = 2A_{CH}\frac{1 - x}{10}\frac{4}{a\omega_{1H}^2}\left(\frac{H - \Delta E}{H + \Delta E}\right)^{1/2}\left[1 + \frac{H - \Delta E}{H + \Delta E}\right]^{-1} \tag{29}$$

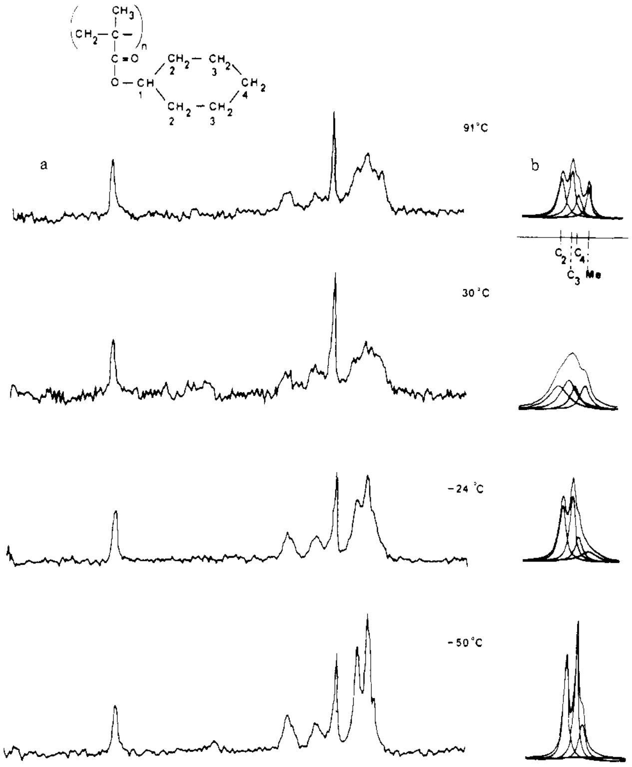

Figure 2. Experimental (a) and simulated (b) 12-MHz MAS CP ^{13}C NMR spectra of solid poly(cyclohexyl methacrylate) at different temperatures.

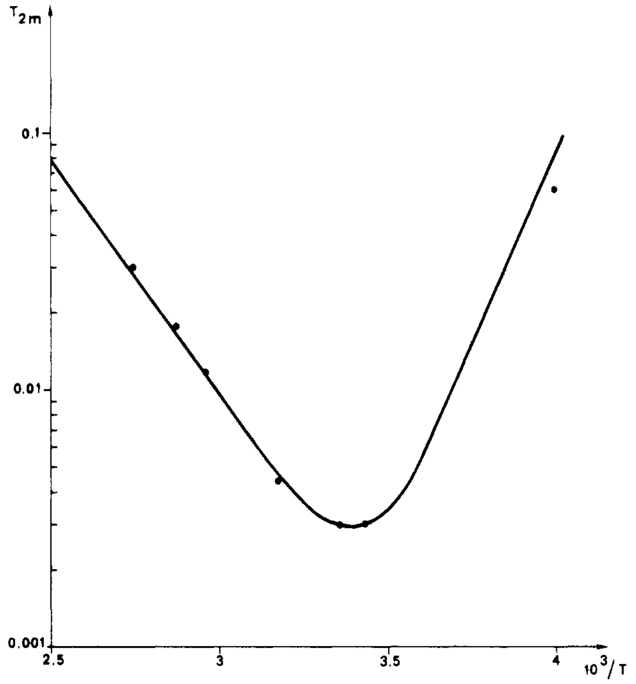

Figure 3. Transverse relaxation times T_{2m} of the methylene ring carbon C2 as a function of $10^3/T$. T is the absolute temperature. The full curve represents calculated values deduced from eq 21.

Results and Discussion

Magic-angle spinning (MAS) cross-polarization (CP) ^{13}C NMR spectra of solid poly(cyclohexyl methacrylate) as a function of temperature are shown on Figure 2a. They consist of several lines which have been identified from left to right, in order of increasing magnetic field, as a line due to the carboxyl carbon, a line due to the methine group of the side ring, a broad line arising from the main-chain methylene group, a line due to the main-chain quaternary carbon, and finally a complex pattern, whose shape depends on temperature, corresponding to the cyclohexyl methylene carbon and methyl carbon resonances. At low temperature (-50 °C) the three cyclohexyl methylene carbon peaks are narrow and well resolved. They are in sharp contrast with the room-temperature spectrum, which is so broadened that the resolution has completely disappeared. Between these two extrema, intermediate features are observed at the other temperatures. This broadening of aliphatic protonated carbon lines, which exceeds a few ppm, together with its characteristic variation as a function of temperature, is a clear indication of modulation of the carbon–proton dipolar coupling by slow motions of the side ring.[1,8]

In order to determine the transverse relaxation times T_{2m}, the broadened cyclohexyl methylene and methyl carbon lines were deconvoluted, using Lorentzian line shapes. The chemical shifts of the three methylene lines were determined from the low-temperature (-50 °C) spectrum; the methyl resonance location was taken from the MAS CP ^{13}C NMR spectrum of poly(cycloheptyl methacrylate).[1] As the experimental MAS CP ^{13}C NMR spectra were recorded under the condition of optimum carbon–proton contact time, the intensity of the individual lines was assumed to be proportional to the number of resonant carbons.

Comparison of experimental and simulated spectra is shown on Figure 2. T_{2res} was estimated as 6×10^{-3} s from the methylene ring carbon line width of poly(cycloheptyl methacrylate) recorded under similar experimental conditions.[1] In this polymer at room temperature, the ring motions have proved to be very rapid processes, having too high a frequency to broaden the corresponding line widths of MAS CP ^{13}C NMR spectra,[1] and therefore the line widths of the methylene ring carbon peaks are purely static in origin. Besides, comparison of the poly(cycloheptyl methacrylate) spectrum with the poly(cyclohexyl methacrylate) spectrum at -50 °C shows that the ring carbons in these two polymers experience very similar static chemical shift dispersion effects.

The transverse relaxation time T_{2m} of the methylene ring carbon C2 thus obtained is reported on Figure 3. (Numeration of the ring carbons of poly(cyclohexyl methacrylate) is given in Figure 2). Its dependence on temperature is similar to that of the theoretical curve predicted by formula 2. The T_{2m} minimum is observed around 20 °C, which indicates that at this temperature the correlation times of the ring motion are of the order of 5×10^{-6} s. As shown on Figure 2, very similar results are observed for the methylene ring carbon C3. The line of the C4 ring carbon seems to be less broadened than those of carbons C2 and C3 as pointed out by simulated spectra plotted on Figure 2. However, results relative to this latter line are not precise enough to make safe conclusions concerning the C4 carbon. Moreover the widths of the main-chain methylene carbon and of the C1 ring carbon lines do not seem to be temperature dependent over the range of temperatures investigated. All these data indicate that the involved dynamical process is a ring motion that mainly affects the C2–H and C3–H internuclear vectors.

These conclusions may be interpreted in terms of the following simple model in which the polymer main chain is fixed while the cyclohexyl ring, which is rigidly bound to the carboxyl moiety, experiences chair–chair inversions as shown in Figure 4. Such a model had already been proposed by Heijboer[11] to account for the mechanical behavior of poly(cyclohexyl methacrylate). Furthermore the choice of a chair–chair inversion had been justified by use of conformational energy calculations.[11] The assumption of the main-chain rigidity is supported by both

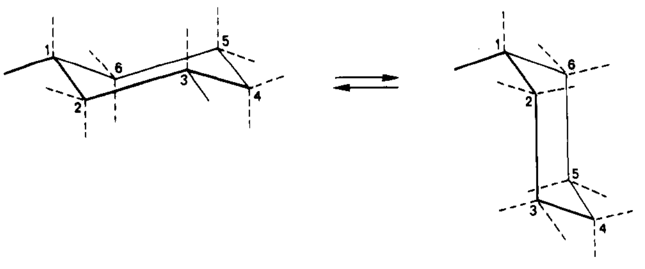

Figure 4. Chair–chair inversion of a cyclohexyl ring with carbon 1 in a fixed position.

the above results and the high value of the glass transition temperature of poly(cyclohexyl methacrylate),[11] which proves that at temperatures under study there is no substantial main-chain reorientation. The cyclohexyl ring is assumed to have tetrahedral angles and equal C–C bond lengths. In the chair–chair inversion described in Figure 4, each of the C2–H and C3–H internuclear vectors performs a 109°28′ rotation about one of the C–C bonds of the ring, which corresponds to a value of x, as defined by formula 17, of $-^1/_3$. Thus this process is able to induce noticeable line broadenings as long as correlation times lie in the range 10^{-4}–2×10^{-7} s. Experimental carbon C2 and C3 line behaviors are in qualitative agreement with the proposed model. Calculations reported above show that, within this model and assuming equal equilibrium populations of the two chair conformations A and B of the cyclohexyl ring, the expected value of T_{2m} at the T_{2m} minimum for the C2 carbon is about 6.3×10^{-5} s. Experimentally the T_{2m} minimum for the C2 carbon is 3×10^{-3} s. Such a difference is accounted for by the inequality of the two potential wells corresponding to each of the chair conformations A and B of the cyclohexyl ring. From the high-temperature slope of the T_{2m} curve (Figure 3) and eq 25, one gets $H - \Delta E \simeq 8.3$ kcal/mol, whereas comparison of calculated values of the T_{2m} minimum as a function of ΔE with the experimental value gives another relation between H and ΔE. Finally one gets $\Delta E \simeq 3.05$ kcal/mol and therefore $H \simeq 11.35$ kcal/mol.

Knowledge of the τ_c value at the T_{2m} minimum calculated from eq 28 leads to the determination of τ_0 defined in formula 12 so that $\tau_0 \simeq 1.65 \times 10^{-14}$ s and

$$\tau_c = 1.65 \times 10^{-14} \exp(H/RT) \qquad (30)$$

The calculated value of T_{2m} from formula 21 and values of x, ΔE, H, and τ_0 determined above are reported on Figure 3. The agreement with experiment over the temperature range of interest is quite satisfying.

Correlation times τ_c calculated from eq 30 are reported on Figure 5 together with data obtained by Heijboer[11] from mechanical measurements. The dependence on absolute temperature T and frequency ν of the loss maximum presented by poly(cyclohexyl methacrylate) was described by an Arrhenius law[11]

$$\nu = \nu_0 \exp(-E_a/RT) \qquad (31)$$

where R is the gas constant, $\nu_0 = 10^{13}$ Hz, and $E_a = 11.3$ kcal/mol. Agreement of results deduced from the two techniques is very good and confirms the conclusions reached by Heijboer,[11] identifying the molecular process responsible for the transition of poly(cyclohexyl methacrylate) as a motional mode of the cyclohexyl ring. However, it must be noticed that the lack of accuracy of data relative to the C4 carbon does not allow us at the present time to fully demonstrate the nature of the molecular mechanism, i.e., the chair–chair inversion, of this ring motion.

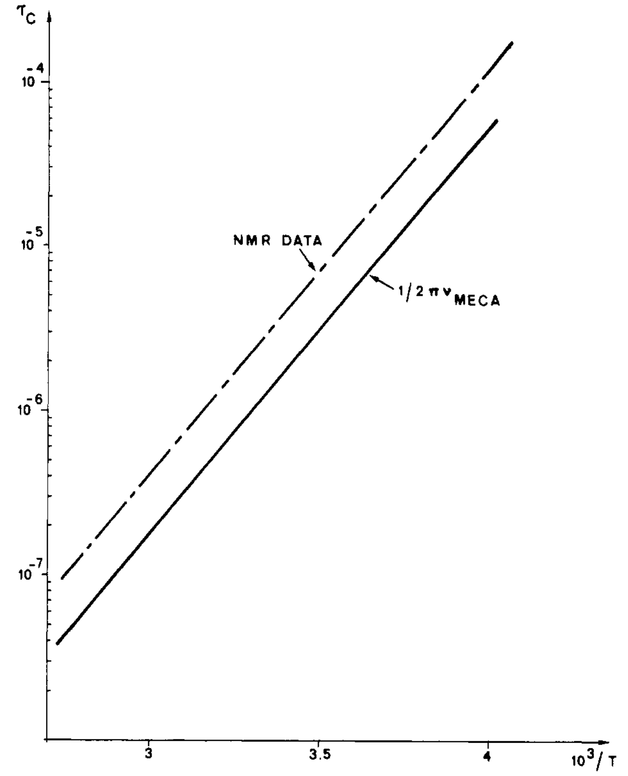

Figure 5. Correlation times τ_c calculated from results reported in Figure 3. NMR results are compared with mechanical data reported in ref 11.

The 3.05 kcal/mol energy difference between the two conformers obtained from NMR experiments is higher than the 0.7 kcal/mol one deduced from conformational energy calculations on an isolated molecule,[11] but it may reflect the role of intermolecular interactions due to molecular packing. From mechanical experiments on various poly(cyclohexyl methacrylate) derivatives,[11] it was also concluded that only a broad distribution of ΔE values, which sharpens with increasing temperature, leads to a temperature dependence of the relaxation strength that does not differ too much from that found experimentally. Such a distribution of ΔE values would of course also explain the rather high value of the observed T_{2m} minimum, but as long as such a distribution is not necessary, it may seem more advisable to use a model whose physical meaning is clearly defined.

It must also be noticed that the methyl line, which is quite narrow at 91 °C, is so motionally broadened at −50 °C that it is not visible on the spectrum. A slow internal rotation of methyl groups is a much more efficient line-broadening mechanism than the cyclohexyl ring inversion, since it averages most of the high intramethyl carbon–proton dipolar interaction. From spectra shown on Figure 2, it can be deduced that the internal rotational correlation time of the methyl group is in the range 10^{-7}–10^{-8} s at −50 °C. This result is compatible with proton spin–lattice relaxation time measurements on the same polymer that have pointed out the presence of a T_1 minimum, which was attributed to the methyl rotation, in the neighborhood of 0 °C for an observing frequency of 50 MHz.[12]

Registry No. Poly(cyclohexyl methacrylate) (homopolymer), 25768-50-7.

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^{13}C NMR Analysis of Microstructure in the Highly Piezoelectric Copolymer Vinylidene Cyanide–Vinyl Acetate

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ABSTRACT: The microstructure of vinylidene cyanide–vinyl acetate copolymer was studied by 125-MHz ^{13}C NMR spectroscopy. Compositional sequence distributions obtained from cyanide (VDCN-centered) and methyl (VAc-centered) triads were in good agreement with the predicted sequence distributions calculated by using the reactivity ratios (r_1, r_2) and the conditional probabilities for cross propagation (P_{12}, P_{21}). Configurational results in the alternating sequence were interpreted in terms of our defined ϵ-enchainments (those of a group relative to the other separated by five skeletal carbons) assuming VAc–VDCN as a repeating unit. ϵ-Isotacticity σ_ϵ could be obtained from cyanide carbon resonance as well as from methine carbon resonance, showing good agreement with each other. It was found that vinylidene cyanide–vinyl acetate copolymer is a highly alternating copolymer with a nonstereoregular structure.

Introduction

It is well-known that crystalline polymers having large dipole moments in the side chains can exhibit piezoelectric properties if the main chains have an all-trans conformation (planar zigzag structure) and if the crystal structure shows a spontaneous polarization. Poly(vinylidene fluoride) has received major attention in the polymorphism of the crystalline structure because its electrical properties are closely related to the crystalline structure.[1,2] Much interest has recently been also centered on the copolymer of vinylidene fluoride and trifluoroethylene. The conformations of the copolymer may be transformed into a well-ordered planar zigzag phase from a mixture of disordered trans-planar and 3/1-helical phases by mechanical or electrical treatments, resulting in a ferroelectric to paraelectric phase transition.[3,4]

Recently, we found fairly good piezoelectric activity in a copolymer of vinylidene cyanide and vinyl acetate (hereafter, an abbreviation is used: P(VDCN–VAc)). This copolymer, however, seems to be almost amorphous because no melting is observed by DSC and it has broad X-ray reflections at $2\theta = 15°$ and $2\theta = 30°$.[5] Infrared absorption at 2240 cm^{-1} corresponds to the stretching vibration of the C≡N group. From the poling time dependence of the absorbance of this band the origin of the marked piezoelectric behavior is deduced to be the rotation of the C—C≡N group, the dipole moment of which is 4.0 debye.[6] As reported in the previous paper,[7] there is another interesting phenomenon in P(VDCN–VAc). This is a noticeable enthalpy relaxation in the region of the glass-transition temperature (T_g). By isothermal annealing below T_g, enthalpy relaxation toward the equilibrium glassy state appears whereas glasses usually exist in a nonequilibrium state.[8] For P(VDCN–VAc) structural changes during enthalpy relaxation correspond to molecular motions relevant to the dipolar rotation of C—C≡N groups. Therefore, during poling in a high dc electric field, the cyanide group is believed to orient to some extent also in the amorphous phase because of the existence of finite free volume.

The molecular structures of piezoelectric polymers have been considered as one of the most important factors in determining piezoelectric activity. Molecular conformation is especially important, as well as chain structure, in understanding the origin of piezoelectricity not only in crystalline but also in amorphous polymers. For crystalline poly(vinylidene fluoride), Douglass[9,10] and his co-workers have provided useful information on the macroscopic dipole orientation with respect to the poling direction by observing the NMR line-width anisotropy. Their NMR results are in agreement with those of X-ray studies. However, the origin of the piezoelectricity in amorphous polymers has not yet become fully understood because of the lack of structural information concerning the amorphous material.

Generally, high-resolution NMR spectroscopy has been the very effective means for the elucidation of the microstructure of synthetic polymers.[11,12] In the present work, ^{13}C high-resolution NMR spectra of a P(VDCN–VAc) sample have been obtained for the first time with spectrometers operating at 25 and 125 MHz. The higher field NMR spectrum has been particularly successful in providing detailed information on the monomer sequence distribution and the stereochemical configuration of P(VDCN–VAc) copolymer.

Experimental Section

Materials. The vinylidene cyanide (VDCN) was prepared from bi(acetyl cyanide).[13] The copolymer of vinylidene cyanide and vinyl acetate (VAc) was synthesized by radical polymerization

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