Fellowship. Invaluable discussions with Professors C. W. Frank and M. D. Ediger and with Dr. J. Baumann as well as the members of the Stanford Center for Materials Research Polymer Thrust Program are gratefully acknowledged.

Registry No. (2-VN)(MMA) (copolymer), 53640-71-4; PMMA, 9011-14-7.

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^{13}C NMR Study of the α-Methyl Group Rotation in Solid Poly(methyl methacrylate): Detection of the ^{13}C T_1 Minimum

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Received September 12, 1986

ABSTRACT: The ^{13}C spin–lattice relaxation time of α-methyl groups in amorphous poly(methyl methacrylate) (PMMA) has been measured in the temperature range 193–388 K in two quenched samples with different tacticities. Both samples were predominantly syndiotactic, with 72.5% (s-PMMA) and 49.5% syndiotactic triads (si-PMMA). In both cases the T_{1C} minimum was observed: centered around 160 K with nT_{1C} = 300 ms (si-PMMA) and centered around 275 K with nT_{1C} = 200 ms (s-PMMA). (n denotes the number of protons directly bound to the carbon in question.) Differences in T_{1C} values as well as distinctly different shapes of the (nT_{1C}, K/T) curves result from different sample tacticities. We propose that the high values of T_{1C} measured at the minima result from the superposition of the α-methyl group motion and rapid fluctuations of the main chain.

Introduction

The rotation of side chains in poly(methyl methacrylate) (PMMA) has been investigated over a wide temperature range by the following techniques: dielectric[1] and dynamic mechanical relaxation,[2] pulsed ^1H NMR,[3] broad-line NMR,[4] and both inelastic and quasielastic neutron scattering.[5-7] Studies of the α-methyl group rotation about its C_3 axis are incomplete and often contradictory despite a large body of ^{13}C NMR data which already exists. Such measurements have normally been made on stereoregular PMMA both in solution[8,9] and in the solid state[10-12] at room temperature and above; this temperature range limits the amount of useful information obtainable. The preliminary quasielastic neutron scattering investigations were similarly restricted to high temperatures because the rotation of the α-methyl group is scarcely accessible to neutrons for reasons of resolution.[6]

^{13}C NMR studies conducted over a wide temperature range can provide the necessary information since they allow selective observation of a chosen resonance line in the solid state. Moreover, both the ^{13}C spin–lattice relaxation time T_{1C} and the chemical shift anisotropy serve as sensitive probes of molecular motion in localized environments.[13-15] The quantities characterizing rotational motion, rotation rates and the activation energy, can be confidently determined from the (nT_{1C}, K/T) plots pro-

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0024-9297/87/2220-0175$01.50/0

vided that the T_{1C} minimum can be detected. (n denotes the number of protons directly bound to the carbon in question.) However, such a minimum has not yet been observed for any methyl group, supposedly for reasons of the broadening of the methyl carbon resonance line.[16] We did not expect such an argument to apply to the α-methyl group in PMMA and so report here the detection of T_{1C} minima for two solid PMMA samples with different tacticities.

Experimental Section

^{13}C spin–lattice relaxation times T_{1C} and high-resolution solid-state ^{13}C spectra were measured with a JEOL JNM-FX200 pulse FT NMR spectrometer equipped with a CP/VT high-power probe under a static magnetic field of 4.7 T. The resonant ^{13}C frequency was 50.2 MHz. Samples were cooled with nitrogen gas in the temperature range 193–300 K and heated with compressed air above 300 K; in both cases the temperature stability was ±1 K.

^{13}C spin–lattice relaxation times T_{1C} were measured for the α-methyl group by using a slightly modified inversion–recovery π-τ-$\pi/2$ pulse sequence. The typical $\pi/2$ pulse width was 3 μs. The radio-frequency field strength $\gamma B_1/2\pi$ used for dipolar decoupling (DD) was 59 kHz. The time intervals τ between the π and $\pi/2$ pulses were in the range 10–260 ms. During this period a train of ^1H $\pi/2$ pulses separated by 5 ms was employed to saturate ^1H magnetization. Repetition of these pulse sequences was delayed for at least $5T_{1C}$'s of the α-methyl carbon. Since T_{1C}'s of other carbons are much longer,[12,23] this procedure enabled us to suppress the contributions from their resonance lines. Liquid benzene was used as an external reference (128.5 ppm from tetramethylsilane (Me_4Si)).

The samples used were predominantly syndiotactic poly(methyl methacrylate) of high molecular weight. The triad sequences were determined to be 34.8% isotactic, 49.5% syndiotactic, and 15.7% heterotactic (si-PMMA) and 4.9% isotactic, 72.5% syndiotactic, and 22.6% heterotactic (s-PMMA) by solution-state ^1H NMR spectroscopy. Samples were hot-pressed at approximately 400 K under 138-MPa pressure into thin films and quenched in cold water as required for neutron scattering measurements. Subsequently these films were broken into small pieces and loaded into NMR tubes.

Results and Discussion

Figure 1 shows typical stacked spectra of s-PMMA recorded at 303 K (top) and 193 K (bottom). The relaxation process of the α-methyl carbon line, which appears around 21 ppm, can be selectively observed at both temperatures, although some minor contributions from other carbons with much longer T_{1C}'s still remain downfield. Two small upfield peaks are likely to be an artifact coming from probe materials, because those peaks appeared also for blank measurements using an empty NMR glass tube. Conventional decay curves obtained from peak heights of the α-methyl lines were initially exponential, although some deviation appeared at the later stage because of the contribution from much longer T_{1C} components.[12,23] T_{1C} values of the α-methyl carbons could be calculated from the initial slopes with an accuracy of 10–20%.

Figure 2 shows ^{13}C spin–lattice relaxation times plotted as nT_{1C} as a function of $1/T$ for s-PMMA and si-PMMA. In both cases broad, but marked minima are visible, though the curve for s-PMMA is shifted to a higher temperature and has a more clearly defined minimum. The values of T_{1C} at the minimum, $(T_{1C})_{min}$, differ in the two cases: 200 ms for s-PMMA and 300 ms for si-PMMA. We ascribe these differences to the influence of the enrichment of syndiotactic triads in s-PMMA. It is well established that the potential hindering α-methyl group rotation in isotactic PMMA and syndiotactic PMMA is lower than and equal to 32 kJ mol^{-1}, respectively.[5,6] Therefore, it is reasonable to conclude at least that such slower reorientation of α-methyl groups in s-PMMA is associated with the appearance of the T_1 minimun at higher temperature for this sample.

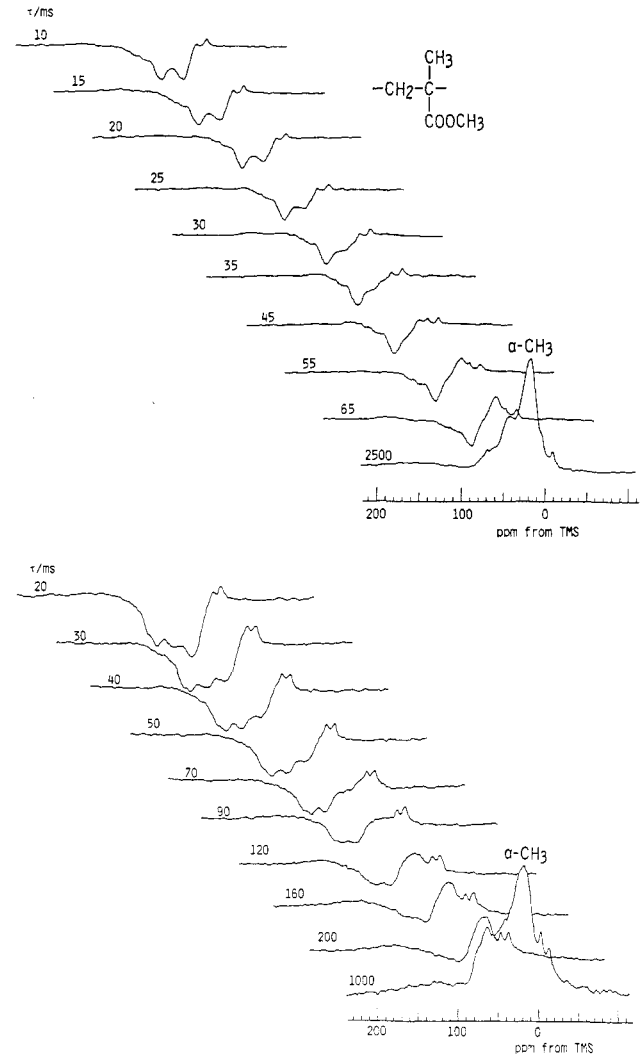

Figure 1. Stacked spectra of s-PMMA taken at 303 K (top) and 193 K (bottom).

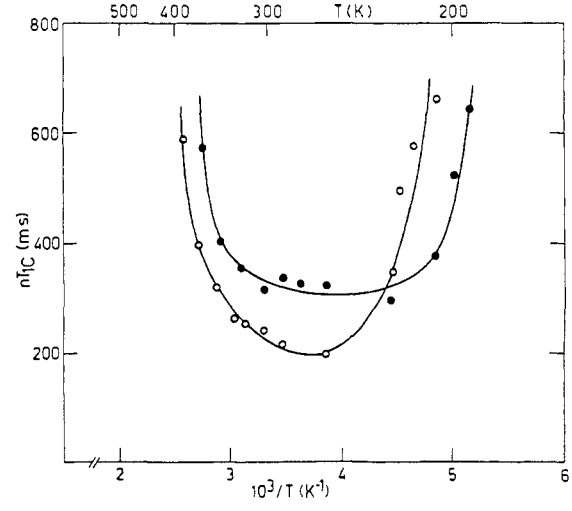

Figure 2. ^{13}C nT_1 for s-PMMA (○) and si-PMMA (●) as a function of $1/T$.

We attribute the appearance of T_{1C} minima in the T^{-1} curves (Figure 2) to the onset of α-methyl group rotation with a correlation time τ_c of the order of 10^{-9} s. Generally, a minimum of the kind shown in Figure 2 appears when

the correlation time τ_c of molecular motion becomes of the order $1/\omega_c$, ω_c being the Larmor frequency of the ^{13}C nucleus.[17] For the value of $\omega_c = 2\pi \times 50$ (MHz) used in this experiment, $\tau_c \simeq 3 \times 10^{-9}$ s, in good agreement with the value of τ_c obtained for the α-methyl group rotation from quasielastic neutron scattering measurements[6] and with the value estimated from the ^1H NMR spin–lattice relaxation time T_1 studies.[3]

One particular problem remains. Why are the values of $(T_{1C})_{min}$ so extraordinarily high for both samples? They can neither be rationalized with a single correlation time mode nor explained in terms of any wide distribution of correlation times. But if one assumes that the T_{1C} minima observed are caused by a superposition of two motions, then the high values of $(T_{1C})_{min}$ can be understood in terms of picosecond fluctuations of the PMMA backbone. Since the α-methyl group is bound directly to the main chain, the hypothesis of the superposition of the backbone motion on the α-methyl rotation is a plausible one. Heatley and Begum have found a linking between the side α-methyl group and the main-chain motion in PMMA in solution.[8] Significant increases of T_{1C} in proteins due to atomic fluctuations on the picosecond scale have been reported by Levy and Karplus.[18] The possibility of such motion occurring in a glassy polymer below its glass transition temperature finds some support also in other investigations: thus an application of Howarth's 3-τ model[19] to solid polyethylene and polyesters above T_g has yielded similar values of the correlation times of the backbone motion.[20,21] Recent neutron scattering experiments conducted on several rubbery polymers also show the presence of picosecond fluctuations of the main chain.[22]

It is remarkable that the T_{1C} minimum due to rotation of the methyl group has not been detected so far. One of the reasons quoted in the literature[16] was the broadening observed in solid polypropylene (PP) at low temperatures. It was attributed to the onset of methyl group rotation around the C_3 axis with a frequeency comparable to the strength of the proton dipolar decoupling field.[16] This explanation does not seem plausible to us for several reasons. First, the field strength of the order of 10^5 Hz used by Fleming et al. is too low for a frequency of the methyl rotation above the temperature of the T_{1C} minimum. From the neutron scattering studies by Allen et al.[5] the activation energy for the methyl group rotation in PP is $E_a = 12.2$ kJ mol^{-1}.[5] This yeilds a corresponding correlation time τ_c shorter than 10^{-8} s and subsequently a frequency of motion well above the field strength of 10^5 Hz. It is noteworthy that the resonance lines of the CH and CH_2 carbons, which have a mobility lower than that of the CH_3 carbon, do not disappear at higher temperatures. Therefore elucidation of the cause of the broadening of the methyl resonance line in PP requires detailed studies of the possible CP and MAS effects. It is also clear why the T_{1C} minima in solid PMMA are observed without broadening: there is not molecular motion with a frequency comparable to the ^1H dipolar decoupling field strength in the temperature range where these minima appear.

Conclusions

In order to explain the observed value of T_{1C} minima in both PMMA stereoisomers, we have proposed an extension of the 3-τ model. This amounts to introduction of a motion with τ_c in the picosecond range, which is superimposed on the α-methyl group motion. Such a superposition describes a linking of local backbone and side-chain motions. This hypothesis is currently under investigation, and further ^{13}C NMR studies on a purely isotactic PMMA are being carried out.[23]

Acknowledgment. We thank Dr. J. S. Higgins for helpful discussions and Dr. D. A. Young for a critical reading of the manuscript. B.G. is indebted to the Royal Society for financial support and thanks Kyoto University for its hospitality during a study stay in Japan. She is also grateful to Prof. W. T. Welford (Imperial College) for his help and continuous encouragement throughout the course of this project.

Registry No. PMMA, 9011-14-7.

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