Polymer Bulletin 5, 255-261 (1981)

Polymer Bulletin

^{13}C NMR Spin-Lattice Relaxation in Solid Poly(Methyl methacrylate)

Effects of Tacticity and of Plasticizers

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Presented at the 22nd Microsymposium, "Characterization of Structure and Dynamics of Macromolecular Systems by NMR Methods", Prague, July 20-23, 1981

SUMMARY

^{13}C spin-lattice relaxation rates R_1 in samples of solid PMMA have been measured with CP MAS NMR. Isotactic, atactic, syndiotactic, and the 1:2 i-s PMMA complex were measured, along with atactic samples containing bisdioxan or the monomer as a plasticizer. The reorientation of the α-methyl protons is the dominant relaxation source for the methylene, α-methyl and quarternary carbon nuclei. Increased mobility of the polymer in the presence of a plasticizer is not reflected in significant changes in R_1.

INTRODUCTION

The combination of the NMR techniques of ^{13}C-{^{1}H} cross-polarization (CP) (PINES et al., 1973), of fast magic angle spinning (MAS), and of strong dipolar decoupling (DD) of the protons during acquisition of the ^{13}C FID signal, has made it possible to obtain high-resolution ^{13}C NMR spectra of polymers in the solid state (SCHAEFER and STEJSKAL, 1976; LYERLA, 1979; GARROWAY et al., 1979). The spectra are usually well resolved, and the spin-lattice relaxation rate can be measured for each individual resonance peak. In particular, both the relaxation of the carbon atoms on the polymer backbone and of those on side chain groups can be followed separately. Since the spin-lattice relaxation rates are sensitive to local motions, it is possible, in principle, to probe separately the motions of the side chain groups and of the polymer backbone.

The mechanical properties of a solid polymer are related to motions of the polymer molecules. Both the tacticity and the presence of a plasticizer have a profound effect on the mechanical properties of poly(methyl methacrylate), PMMA. We here report the effect of tacticity and of plasticizers on the ^{13}C spin-lattice relaxation rates R_1 in solid PMMA. $R_1=T_1^{-1}$, where T_1 is the spin-lattice relaxation time. The main effect of a plasticizer is expected to be an enhanced mobility of the polymer chain. R_1 values are most sensitive to motions which occur at a rate comparable to the NMR frequency, i.e. to motions in the range of 10^7-10^{10} Hz. Therefore, the measurement of spin-lattice relaxation rates in the rotating frame, $R_{1\rho}$, might seem to offer a more sensitive way to probe changes in the mobility of the polymer backbone. However, if $R_{1\rho}$ is measured under CP MAS NMR conditions, no simple and straightforward relation exists with the slower molecular motions (GARROWAY et al., 1979; VanderHART and GARROWAY, 1979). For that reason, $R_{1\rho}$ measurements are not included here.

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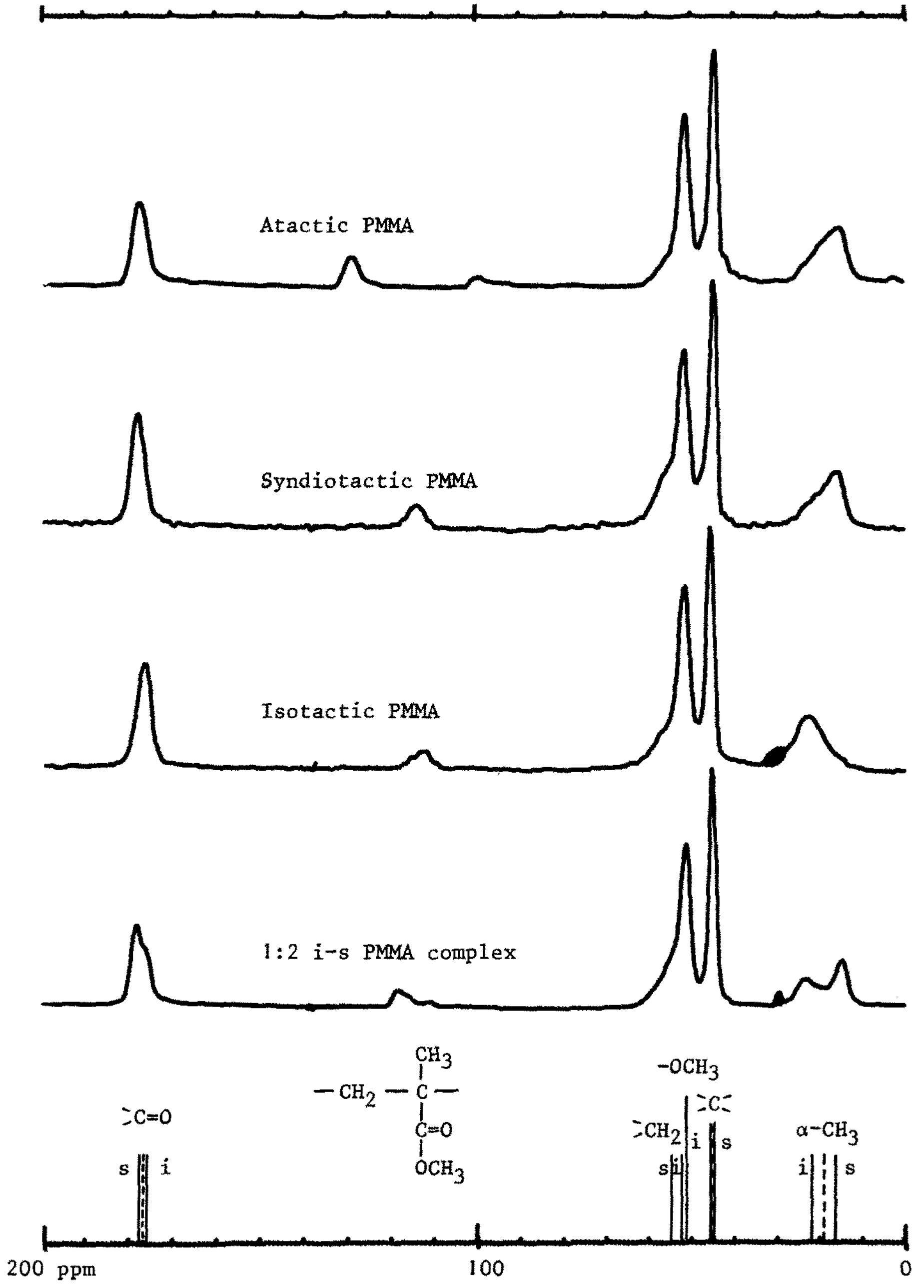


FIGURE 1. ^{13}C CP MAS NMR spectra of solid PMMA at room temperature. The peaks between 90 and 130 ppm are spinning sidebands; black peaks in the α-CH_3 region are ascribed to trapped solvent molecules. The stick spectrum shows the resonance positions in solution. i: isotactic dyad (m) or triad (mm) resonances; s: syndiotactic dyad (r) or triad (rr) resonances; broken lines: heterotactic triad (mr) resonance.

EXPERIMENTAL

^{13}C NMR spectra and spin-lattice relaxation rates were measured at ambient temperature with a home-built CP MAS NMR spectrometer, operating at a ^{13}C NMR frequency of 45.27 MHz. The pulse sequence programmer (Van OS and VEEMAN, 1979) and the design of the sample spinner accessory (Van DIJK et al., 1980) have been published elsewhere; the doubly-tuned single-coil probe design of STOLL et al. (1977) is used. Cross-polarization and proton dipolar decoupling were achieved with ^{13}C and ^{1}H RF magnetic field strengths of 35 kHz. A CP contact time of 1 ms was used, and the sample spinning rates ranged from 2.4 to 3.0 kHz.

^{13}C spin-lattice relaxation rates were measured with a slightly modified version of the T1CP method described by TORCHIA (1978). This method has distinct advantages over the inversion-recovery method for the measurement of slowly relaxing ^{13}C resonance: the final equilibrium magnetization does not need to be measured, since the T1CP relaxation decay tends to zero for long relaxation delays; and, a slowly relaxing background signal from the Kel-F spinner and the coil surroundings, which hampers an accurate determination of peak amplitudes in the inversion-recovery experiment, is completely absent in the T1CP relaxation curves. The proton magnetization was kept saturated during the relaxation delay time by applying a train of short pulses at the proton NMR frequency (2 μs repetition rate; 15% duty cycle).

Spin-lattice relaxation rates were determined from a least-squares fit of the measured peak amplitudes to the relaxation function $A(t)=A(0)\exp(-R_1t)$. Some of the relaxation curves consistently showed non-exponential behavior; in those cases we choose to characterize the decay with the function $A(t)=A(0)\exp(-R_1t(1+fR_1t))$ (BAKAY et al., 1975). This expression is useful to describe slightly non-exponential curves, as long as very long relaxation delay times t are not included. With this function a good fit was obtained to all the measured points of the non-exponential relaxation curves. The spin-lattice relaxation rate R_1 from such a fit describes the initial slope of the relaxation decay; the non-exponentiality factor f characterizes the degree of non-exponentiality.

The PMMA samples studied were of high molecular weight and are listed in TABLE I. The tacticity was determined from ^{1}H spectra of 5% w/v solutions in $CDCl_3$. Bisdioxan and methyl methacrylate were incorporated as a plasticizer. Commercial Perspex was studied in the form of a massive spinner. All other samples were studied in powdered form and packed into Kel-F spinners with a sample volume of .28 cm^3. About 2000 scans were needed to obtain a good signal-to-noise ratio.

RESULTS AND DISCUSSION

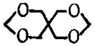
^{13}C NMR spectra. Typical ^{13}C CP MAS NMR spectra of the PMMA samples are shown in FIGURE 1. The plasticizer molecules (bisdioxan or methyl methacrylate monomer) did hardly crosspolarize under our experimental conditions; we ascribe this to the large mobility of the plasticizer molecules.

The CP MAS ^{13}C NMR resonances of PMMA are broad compared to those measured in solution. For comparison, a stick spectrum of the resonance positions of PMMA in solution is included in FIGURE 1 (PEAT and REYNOLDS, 1972; LYERLA et al., 1977). The four functional groups of PMMA are easily assigned, although the $>CH_2$ and $-OCH_3$ resonances overlap. The resonance positions agree with those measured in solution. Fine structure due to

TABLE I. ^{13}C spin-lattice relaxation rates at 45.27 MHz of some solid PMMA samples.

Sample	Tacticity (mm/mr/rr triad ratio)	Source	Relaxation rates R_1 (s^{-1})				
			α-CH_3	$>C=O$	$>CH_2$	$-OCH_3$	$>C<$
Commercial Perspex	4/31/65		19	.10	.10	.16 (f=.07)	.25 (f=.07)
Atactic PMMA	similar	1	20	.10	.11	.16 (f=.05)	.25 (f=.07)
Ibid., + 20% w/w bisdioxan★		1	--	.11	.12	.18 (f=.07)	.28 (f=.07)
Ibid., + 40% w/w bisdioxan★		1	21	.12	.16	.18 (f=.03)	.29 (f=.06)
Ibid., + 10% w/w monomer★		2	--	.11	.14	.19 (f=.06)	.28 (f=.08)
Isotactic PMMA	95/5/0	3	10	.06	.09	.14 (f=.11)	.17 (f=.11)
Syndiotactic PMMA	1/9/89	3	19	.10	.10	.17 (f=.07)	.28 (f=.09)
1:2 i-s PMMA complex	as above	3	11 (i) 19 (s)	.09 (i) .13 (s)	.12	.19 (f=.09)	.27 (f=.08)
Estimated error in the relaxation rates			10%	15%	30%	10% (f:50%)	10% (f:50%)

f characterizes a non-exponential relaxation (see experimental section)

★Bisdioxan = 2,4,8,10-tetraoxaspiro-[5.5]-undecane: 

Monomer = methyl methacrylate, MMA

PMMA Sources: 1. Nijverheidsorganisatie TNO, Delft, The Netherlands

2. Philips Research Laboratories, Eindhoven, The Netherlands

3. Department of Polymer Chemistry, University of Groningen, The Netherlands

differences in the tacticity is not resolved very well: only the isotactic (mm) and syndiotactic (rr) triad resonances of the $\geq$C=O and α-CH_3 group are separated well enough to become identifiable. This is very clear in the spectrum of the stereocomplex of iso- and syndiotactic PMMA. Non-resolved fine structure is a major source of the line broadening of the resonances. In particular the α-CH_3 resonance is rather broad and clearly asymmetric, even in the spectra of the stereoregular samples. One cannot simply assign the three triad resonances; instead, a careful inspection of the line shape seems to hint at a larger number of overlapping lines. We are currently investigating the α-CH_3 region in detail, hoping to identify specific conformations in the solid state. Both the folding of the main chain, and the orientation of the ester group, can give rise to a multitude of lines in the α-CH_3 region.

Spin-lattice relaxation. The measured relaxation rates R_1 are tabulated in TABLE I. The relaxation of the -OCH_3 and $\geq$C$\leq$ carbons proceeds distinctly non-exponential over the experimental range of relaxation delay times t (16 s. maximum). For these lines the non-exponentiality factor f is given as well (see experimental section). α-CH_3 rates were measured from the largest peak amplitude. From changes in the line shape it is clear, however, that the α-CH_3 region does not relax uniformly. In commercial perspex for example, the α-CH_3 relaxation can be decomposed into three differently relaxing components of equal width, and centered at 16, 20, and 23.5 ppm. Relaxation rates of 20, 13, and 19 s^{-1} are measured, with relative intensities of 4:2:1 respectively. It is tempting to identify these components with the α-CH_3 triad resonances. However, the line shapes differ in detail from a simple three-line spectrum, again indicating a multitude of overlapping α-CH_3 resonances. Moreover, the intensity of the component at 23.5 ppm is much larger than is expected for the isotactic (mm) resonance in atactic PMMA.

From TABLE I it is clear, that tacticity has the largest effect on the spin-lattice relaxation rates R_1. The relaxation proceeds considerably slower in isotactic than in syndiotactic PMMA, both in the pure stereoregular samples and in the stereocomplex. Commercial perspex and the atactic PMMA samples behave similar to syndiotactic PMMA. This is to be expected, since samples prepared by free radical polymerization are predominantly syndiotactic. The presence of plasticizers hardly affects the relaxation rates. At most, a slight trend towards faster relaxation occurs.

^{13}C spin-lattice relaxation rates of solid PMMA have been published before. Prelimenary data given by VEEMAN and MENGER (1981) compare to those given here; the present data are more accurate. Spin-lattice relaxation in non-spinning PMMA has been measured by SCHAEFER et al. (1975). Their results differ from the ones presented here.

Comparing the ^{13}C relaxation data with those obtained in solution (LYERLA et al., 1977; HATADA et al., 1977), the most significant change occurs in the $\geq CH_2$ relaxation: in solution, R_1 is about two orders of magnitude larger than in the solid. This clearly reflects the much larger mobility of the polymer backbone in solution. In the solid state, the presence of a plasticizer seems to have the largest effect on the $\geq CH_2$ relaxation. This might arise from an increase in the backbone mobility. Unfortunately the accuracy is not good enough to be very definite about the effect of a plasticizer.

The α-CH_3 relaxation proceeds rapidly. R_1 is close to the theoretical maximum of about 30 s^{-1} for a methyl group (DODDRELL et al., 1972), indicating that the α-CH_3 group reorients at a rate comparable to the NMR (angular) frequency of 3. 10^{+8} s^{-1}. Both in solution and in the solid state, the α-CH_3 relaxation proceeds faster in the syndiotactic than in the isotactic conformation. From other experiments it is known, that the barrier to rotation for the α-CH_3 group is lower in the isotactic conformation, resulting in faster rotation (see LYERLA et al., 1977). Faster rotation, leading to slower relaxation, implies that the α-CH_3 rotation is to the high-temperature side of the R_1 maximum. The α-CH_3 relaxation data are compatible with proton spin-lattice relaxation measurements, where it was shown that the R_1 maximum at a similar NMR frequency occurs near 0°C (SLICHTER, 1966).

In the solid state, the rotation of the α-CH_3 group seems to completely dominate the relaxation of the other carbon nuclei, except for the $-OCH_3$ carbon. This can be concluded from the observed ratio of the relaxation rates. Let us assume that the reorienting methyl protons constitute the only source for dipolar relaxation. The carbon relaxation rates then should be proportional to $\overline{r_{CH}^{-6}}$, where r_{CH} is the carbon-proton distance. The expected R_1 of the $>C<$ carbon, relative to the one of the α-CH_3, follows from a straightforward calculation. r_{CH} equals 2.15 A and 1.09 A, respectively. Thus, the $>C<$ carbon should relax at a rate smaller by a factor of 60, which is in excellent agreement with the measurements. For the $>CH_2$ and the $>C=0$ carbons the calculation of $\overline{r_{CH}^{-6}}$ is not as accurate, because the result depends on the assumed conformation. Nevertheless, one expects these two carbons to have a similar relaxation rate, being somewhat smaller than the one for the $>C<$ carbon because of the still larger distances involved. This is indeed observed. Finally, the relaxation rates should scale in proportion to R_1 of the α-CH_3 group; this agrees with the observed changes in i- and s-PMMA. We now also can explain why a plasticizer has so little effect on the observed relaxation rates. Even if the polymer backbone becomes much more mobile, the backbone motion still occurs at frequencies slow compared to the NMR frequency. Motion of the polymer backbone then contributes relatively little to the relaxation, as compared to the very effective relaxation contribution from the coupling with the α-CH_3 protons.

The $-OCH_3$ carbons seem to be relaxed by their directly-bonded protons. The fast, free reorientation of the ester methyl protons does not yield a very effective relaxation mechanism, but the α-CH_3 protons are far away and contribute even less. This explains why R_1 is rather constant in all measured samples.

CONCLUSIONS

^{13}C spin-lattice relaxation in solid PMMA yield under CP MAS NMR conditions, relaxation rates for each functional group. Except for the $-OCH_3$ relaxaton, the reorientation of the α-CH_3 group seems to be the dominant factor which determines the ^{13}C relaxation in the solid state. The relaxation proceeds slower in isotactic PMMA than it does in syndiotactic PMMA, which is a consequence of faster reorientation of the α-CH_3 group in the isotactic chain. The increase of mobility of the polymer backbone in the presence of a plasticizer is not reflected in a significant change of the spin-lattice relaxation rates R_1.

ACKNOWLEDGEMENTS

We greatly appreciate the help of Dr. J. Heijboer; of Dr. G. Challa, Ir. Y.Y. Tan, and Dr. F. Bosscher; and of Dr. J.G. Kloosterboer, in providing us the samples from sources 3,1, and 2, respectively.

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Received July 9 , 1981
Accepted July 2o, 1981