Solid State ^{13}C NMR Study of Methyl Methacrylate-Methacrylic Acid Copolymers

R. M. Souto-Maior[*]**, M. I. B. Tavares**[†]**, E. E. C. Monteiro**

Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ, Brazil

Abstract: Molecular mobility and comonomer dispersion of copolymers of methyl methacrylate (MMA) and methacrylic acid (MAA) were evaluated through the analysis of the NMR relaxation time constant in the rotating frame ($T_1^H\rho$). Well resolved solid state CP/MAS ^{13}CNMR spectra of PMMA, and two MMA-MAA copolymers were obtained at 75.4 MHz. The spectrum of the homopolymer PMMA presented signals at 16.7, 45.2, 52.2 and 178.1 ppm. Spectra of the copolymers presented the same peaks at essentially the same chemical shifts. Analysis of $T_1^H\rho$ values indicated that the copolymer containing the higher percentage of MAA has better comonomer dispersion along the chain. The experimental values also indicated that the polymers present heterogeneous morphology, having rigid as well as mobile regions.

Resumo: A mobilidade molecular e a dispersão de comonômeros em copolímeros de metacrilato de metila (MMA) e ácido metacrílico (MAA) foram avaliados através da análise da constante de tempo de relaxação no sistema de eixos rotatórios ($T_1^H\rho$). Espectros RMN ^{13}C bem resolvidos foram obtidos para o PMMA e dois copolímeros de MMA-MAA, no estado sólido, pela técnica de CP/MAS a 75.4 MHz. O espectro do PMMA apresentou sinais em 16.7, 45.2, 52.2 e 178.1 ppm. Os espectros dos copolímeros apresentaram os mesmos sinais com os deslocamentos químicos essencialmente iguais aos do homopolímero PMMA. A análise dos valores de $T_1^H\rho$ indicou que o copolímero que contém a maior proporção de unidades de MAA tem a melhor dispersão dos comonômeros ao longo da cadeia. Os valores experimentais também indicaram que os polímeros têm morfologia heterogênea apresentando tanto regiões rígidas como regiões móveis.

Introduction

Poly(methyl methacrylate) (PMMA) and its derivatives, have application in areas as diverse as medicine and engineering.[1] Optical transparency and good mechanical properties are some of the characteristics which render these polymers useful for many practical applications. Since optical transparency is related to the structural organization at the molecular level, and mechanical properties relate to chain dynamics, the study of molecular mobility and structural organization in PMMA and its derivatives are of particular interest.[2,3]

Chain dynamics in polymers and other materials can be studied through the NMR relaxation time constant in the rotating frame $(T_1^H\rho)$.[4] Spin-lattice relaxation in the rotating frame is determined by spatial proximity of nuclei, therefore this parameter gives information about the homogeneity and intermolecular interactions in solid materials.[5]

Here we present results of our work on the study of molecular mobility and comonomer dispersion, through the analysis of solid state ^{13}CNMR spectra and $T_1^H\rho$, of copolymers of methyl methacrylate (MMA) and methacrylic acid (MAA) (Figure 1).

---

[*] End. Atual: Dep. Quím. Fundamental, Universidade Federal de Pernambuco, Recife, Brazil
[†] mibt@ima.ufrj.br
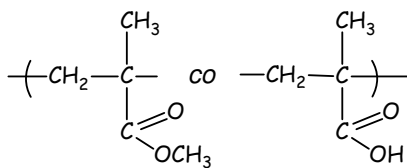
Figure 1. Structure of poly(methyl methacrylate -*co*-methacrylic acid), P(MMA-MAA).

Experimental

PMMA was prepared by suspension polymerization of MMA with 2, 2'-azobisisobutyronitrile as the initiator at 72°C and reaction time of 3 hours. PMAA was prepared through reaction of MAA in the presence of HNO_3 at 30°C. The copolymers, P(MMA-MAA), were obtained through reaction of MMA in the presence of HNO_3 at 30°C. P(MMA-MAA)-24 having 29% of the MAA unity in its structure was obtained after 24 h of reaction time, and P(MMA-MAA)-120 having 43% of MAA was obtained after 120 h of reaction time.[6]

NMR spectra were obtained on a VARIAN Unity Plus 300 spectrometer, operating at 75.4 MHz for ^{13}C. The experiments were performed at ambient probe temperature, using high power decoupling in the gated mode. A zirconium oxide rotor of 7mm diameter was used to acquire the spectra with a spinning speed of 6 kHz at the magic angle (MAS). The MAS ^{13}C NMR spectra were obtained using short delay time (0.3s) between 90° pulses, and CP/MAS ^{13}C NMR was obtained using a 2s delay time.

The variable contact time (VCT) experiment was recorded using the same conditions of the CP/MAS ^{13}C experiment, and the contact time was varied from 0,2 to 8 ms. From the resolved ^{13}C decays $T_1{}^H\rho$ was calculated using the expression:

$$\ln(M_\tau/M_o) = -\tau / T_1{}^H\rho$$

where M_τ is the magnetization at contact time τ, and M_o is the initial magnetization.

Results and Discussion

Well resolved solid state CP/MAS ^{13}C NMR spectra of the homopolymers (Figure 2) and copolymers (not shown here) were obtained. PMMA presented signals at 16.7, 45.2, 52.2 and 178.1 ppm, and PMAA showed signals at 180.7, 53.2, 44.2 and 16.0 ppm. The spectra of the copolymers presented the same peaks as PMMA, at essentially the same chemical shifts. The assignments of the signals on the spectra of homo and copolymers are presented in Table 1 (refer to Figure 1).

Table 1. Assignment of CP/MAS ^{13}CNMR Chemical Shifts of PMMA, PMAA and P(MMA-MAA)

	δ (ppm from TMS)				
	>C=O	-CH$_2$-	-OCH$_3$	>C<	-α-CH$_3$
PMMA	178.1	52.2	52.2	45.2	16.7
PMAA	180.7	53.2	----	44.2	16.0
P(MMA-MAA)-24	178.0	52.3	52.3	45.2	16.9
P(MMA-MAA)-120	178.2	52.5	52.5	45.3	16.8
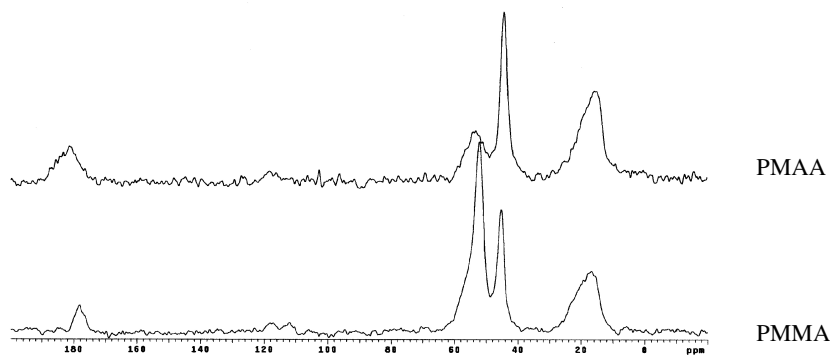
Figure 2. CP/MAS ^{13}C NMR spectra of PMAA and PMMA.

VCT technique made it possible to determine the best contact time for hydrogen-carbon-13 polarization transfer, which was 0.2 ms. The results obtained also allowed the indirect measurement of proton spin-lattice relaxation times in the rotating frame. The results showed slight changes in VCT decay patterns as the proportion of MAA increased in the copolymer (Figure 3).

For PMAA, the signals intensity in the spectra increases with increasing contact time for short values of contact time, followed by an abrupt decrease as contact time increases (Figure3). No signal is detected for contact times of 4 and 8 ms. This characterizes a very rigid material. Besides, all samples showed decay profiles characteristic of rigid materials.
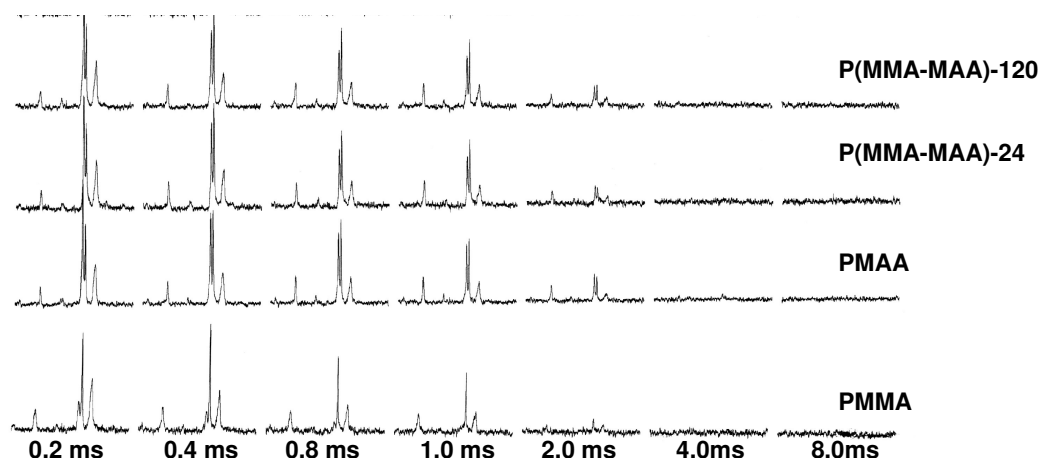
Figure 3. CP/MAS ^{13}C Spectra of obtained at different contact times for PMAA, PMMA, P(MMA-MAA)-24, and P(MMA-MAA)-120.

From the VCT decays $T_1^H\rho$ was determined for each resolved signal (Table 2). The values of $T_1^H\rho$ for protons attached to different carbon

types in P(MMA-MAA)-120 are closer to each other than those of the carbons of P(MMA-MAA)-24. The uniformity of values is due to

uniformity in the chemical environment including spatial proximity of the chains segments. Thus, our results indicate that

P(MMA-MAA)-120 presents better comonomer dispersion along the chain, and consequently a more uniform chain arrangement.

Table 2. Proton spin-lattice relaxation time in the rotating frame ($T_1^H\rho$) for PMMA and MMA-MAA copolymers.

	$T_1^H\rho$ (ms)		
	>C=O	-OCH$_3$ + -CH$_2$	- CH$_3$
PMMA	1.5	1.3	1.2
P(MMA-MAA)-24	1.6	0.9	0.8
P(MMA-MAA)-120	1.3	1.2	1.1

The rapid relaxation for all protons indicates a closely packed structure and therefore a rigid material. On the other hand, MAS spectra (not shown) of all polymers studied have shown signals for all carbons. Also, since the conditions for the experiment were set so that it would provide only signals from the mobile segments of the polymer, one can infer that the polymers also possess regions of high mobility.

Conclusions

MAS and CP/MAS ^{13}CNMR spectra for PMMA, PMAA and copolymers of methyl methacrylate and methacrylic acid, P(MMA-MAA)-24 and P(MMA-MAA)-120, were recorded, and $T_1^H\rho$ values for these polymers measured from VCT experiments. From the spectra and $T_1^H\rho$ values, it could be inferred that both copolymers, as well as the corresponding homopolymers, presented both high and rigid mobility regions, low mobility ones. It could also be deduced that the copolymer with the highest content of the MAA unit (P(MMA-MAA)-120) presented better distribution of comonomers along the chain.

References

1. Salamone, J. C. ed.; *Concise Polymeric Materials Encyclopedia*; CRC Press, 1999.
2. C. R. E. Mansur, M.I. B. Tavares, E. E. C. Monteiro, *J. Appl. Polym. Sci.* **75** (2000) 495.
3. C-F. Huang, F-C. Chang, *Polymer* **44** (2003) 2965.
4. J. Schaefer, E. O. Stejskal, R. Buchdahl, *Macromolecules* **10** (1977) 384.
5. V. J. McBrierty, K. J. Packer, *Nuclear Magnetic Resonance in Solid Polymers (Cambridge Solid State Science Series*; Cambridge University Press, 1993.
6. C.R.E. Mansur, E.E.C. Monteiro, *J. Appl. Polym. Sci.* **68** (1998) 345.