Nuclear Magnetic Resonance Determination of the Effect of End-Capping Ratio on the Structure of Bisphenol A Polycarbonate–Poly(dimethylsiloxane) Block Copolymers

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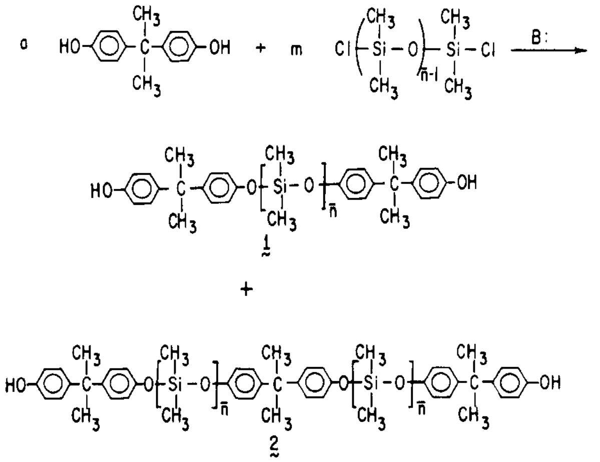
ABSTRACT: Carbon-13 nuclear magnetic resonance spectroscopy has been used to determine the effect of end-capping ratio (molar ratio of bisphenol A to dichlorosiloxane fluid) on the polycarbonate block length in bisphenol A polycarbonate–poly(dimethylsiloxane) block copolymers. Substantial deviations from design block lengths were found for polymers prepared with low end-cap ratios. The reasons for these deviations are discussed.

The block copolymers of bisphenol A polycarbonate (BPAC) and poly(dimethylsiloxane) (PDMS) exhibit a wide range of physical properties, depending upon composition.[1] In a previous paper[2] we described a NMR method for the complete analysis of these copolymers, including composition, average block lengths, and some details of the polymer microstructure. We now demonstrate that this method can be applied to materials prepared with different end-cap ratios (a/m, eq 1)[3] to show the effect of this variable on the structure of the copolymer.

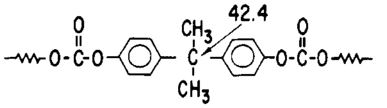
The synthesis of these polymers is carried out in two steps.[3] In the first step bisphenol A (BPA) is reacted with an α,ω-dichloropoly(dimethylsiloxane) fluid in the presence of an acid acceptor such as pyridine. The products depend on the molar ratio of the two components ([BPA]:[dichlorosiloxane], a/m), with both BPA end-capped fluids **1** and higher oligomers, such as **2**, possible (eq 1).[3] The oligomeric fluid is then reacted with additional BPA and phosgene to produce the desired copolymer. The composition and eventual sequence length distribution vary depending upon the total amount of each component used in the synthesis, the average degree of oligomerization of the α,ω-dichloropoly(dimethylsiloxane) fluid ($\bar{n}_D$), and the end-capping ratio (a/m). The expected average BPAC block length ($\bar{n}_X$) can be calculated from $\bar{n}_D$, a/m, and the known amounts of additional BPA and phosgene used.[3]



(1)

^{1}H NMR may be used to determine $\bar{n}_D$ in both the fluids and the polymers since the ^{1}H chemical shifts of the terminal silicon methyl protons in the silicone sequences differ from those of the internal protons.[3] The calculation of $\bar{n}_X$ from $\bar{n}_D$, a/m, and overall polymer composition is subject to uncertainties introduced from either variations occurring during synthesis or errors in determining $\bar{n}_D$ from which a/m is calculated. This is particularly true for materials prepared with a low end-cap ratio since very small changes in a/m cause large changes in $\bar{n}_X$. The ability to fully characterize the polymer enables the relationship between composition and structure to be more accurately determined. In this study a series of six copolymers were analyzed by ^{13}C NMR. All were nominally 50 wt % DMS; three had PDMS block lengths $\bar{n}_D = 9.3$ and three had $\bar{n}_D = 18.4$. Within each series of constant $\bar{n}_D$, three polymers prepared with different end-cap ratios (4, 2, and 1.2) were examined.

Figure 1 shows the ^{13}C NMR spectrum of a BPAC–PDMS block copolymer, with the resonances arising from the BPA quaternary aliphatic carbons expanded to show the fine structure. As previously reported,[2] this region of the spectrum contains all the information needed to determine the polycarbonate block length ($\bar{n}_X$) as well as the amount of BPA which has been incorporated as single units between two silicone blocks. The resonance at lowest field (42.4 ppm) corresponds to the BPA units within the polycarbonate block ("internal"). Replacing a carbonate linkage with a silicone block has an additive shielding effect of 0.4 ppm, to give chemical shifts of 42.0 and 41.6 ppm for the terminal and isolated BPA units, respectively.



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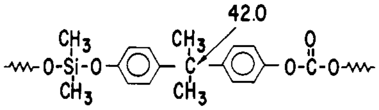

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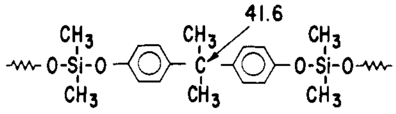


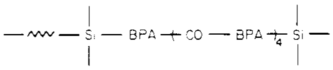
ISOLATED

Figure 2 shows this region of the ^{13}C NMR spectrum for the series of polymers prepared with the same overall composition (50 wt % siloxane) and poly(dimethylsiloxane) block length ($\bar{n}_D = 9.3$) but three different end-cap ratios. The effect of changing the end-cap ratio is apparent in the spectra. If the end-cap ratio is high ($a/m = 4$), as in A, the excess BPA used in the end-capping reaction serves to produce more oligomers of structure 1 than 2, and thus the number of isolated BPA units in the final polymer is small. The BPAC blocks are correspondingly smaller since (at constant composition) more of the total BPA has been used up in the end-capping step for this sample than for a polymer prepared with a lower end-cap ratio (B or C). In materials prepared with a low end-cap ratio ($a/m = 1.2$),

Table I
Distribution of BPA Units and Polycarbonate Block Lengths as a Function of End-Capping Ratio[a]

			BPA units				block lengths		
sample	$\bar{n}_D$	a/m	% internal	% terminal	% isolated	% terminal/ % isolated	$\bar{n}_X$(calcd)[b]	$\bar{n}_X$(corr)[b,c]	$\bar{n}_X$(^{13}C)[b]
A	9.3	4.0	47.5	45.0	7.5	6.6	3.5	4.3	4.1
			47.2	47.0	5.8	8.1			4.0
B	9.3	2	56.0	31.7	12.3	2.6	4.8	5.7	5.5
			56.8	31.4	11.8	2.7			5.6
C	9.3	1.2	60.1	18.2	21.8	0.8	12.3	15.2	8.6
			59.4	18.6	22.0	0.8			8.4
D	18.4	4	74.9	23.2	1.9	6.0	7.0	9.0	8.5
			74.2	22.4	3.4	6.6			8.6
E	18.4	2	79.1	15.3	5.6	2.7	9.9	12.8	12.3
			79.8	15.1	5.1	3.0			12.6
F	18.4	1.2	81.4	9.2	9.4	1.0	27.2	37.0	19.8
			85.5	7.8	6.6	1.2			23.8

[a] All samples were nominally 50 wt % siloxane. [b] Block lengths include the BPA unit at the end of the block: e.g.,



$-\!\sim\!-\mathrm{Si}-\mathrm{BPA}\!+\!\mathrm{CO}-\mathrm{BPA}\!+_4\mathrm{Si}-\!\sim$

(n_X = 5). [c] Corrected to account for actual percent siloxane as measured by silicon analysis.

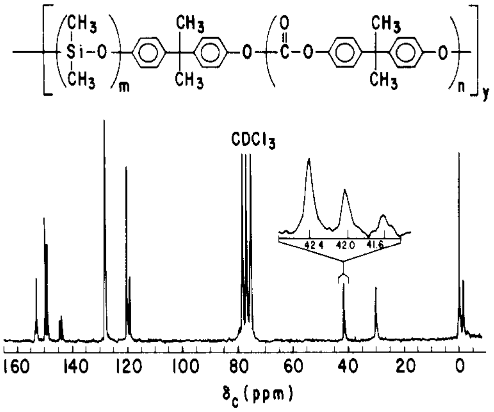


Figure 1. ^{13}C NMR spectrum of a BPAC-PDMS block copolymer (50 wt % PDMS, $\bar{n}_D$ = 9.3, a/m = 2), with the BPA quaternary aliphatic carbon region expanded to show internal (42.4 ppm), block terminal (42.0 ppm), and isolated (41.6 ppm) BPA units. Chemical shifts are given in ppm relative to Me_4Si as calculated from the chloroform-d (δ 76.91) internal reference.

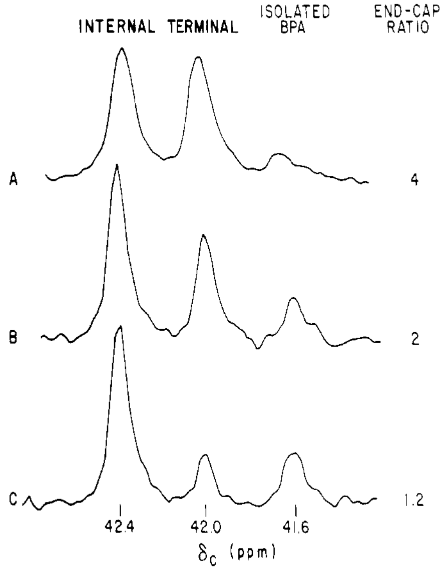


Figure 2. Expansion of the BPA quaternary aliphatic carbon region of the ^{13}C NMR spectrum for three BPAC-PDMS block copolymers (50 wt % PDMS, $\bar{n}_D$ = 9.3) which differ only in end-capping ratio.

as in C, the copolymer consists of longer BPAC blocks and longer PDMS-BPA oligomers. Similar results were obtained for the series of polymers with average PDMS block length $\bar{n}_D$ = 18.4. Figure 3 shows a comparison between samples with the same composition and end-cap ratio, but differing in PDMS block lengths. Spectra B and C are the same as those shown in Figure 2 (50 wt % siloxane, $\bar{n}_D$ = 9.3, a/m = 2 and 1.2, respectively). Spectra E and F correspond to polymers which have $\bar{n}_D$ = 18.4 and the same composition and end-cap ratio as B and C (a/m of B = E = 2, C = F = 1.2). Clearly, the BPAC block lengths are longer for the materials which start with longer PDMS blocks (compare B with E and C with F). The ratio of terminal to isolated BPA units is, however (as expected), roughly the same for materials prepared with the same end-cap ratio (see Table I).

In addition to these data, the polycarbonate block lengths, $\bar{n}_X$, measured from quantitative ^{13}C spectra of the six polymers and the values expected from the stoichiometry (see ref 3 for equations) are collected in Table I along with the distribution of BPA as internal block, block terminal, and isolated units, respectively. The block length, corrected for actual percent silicone, is also included

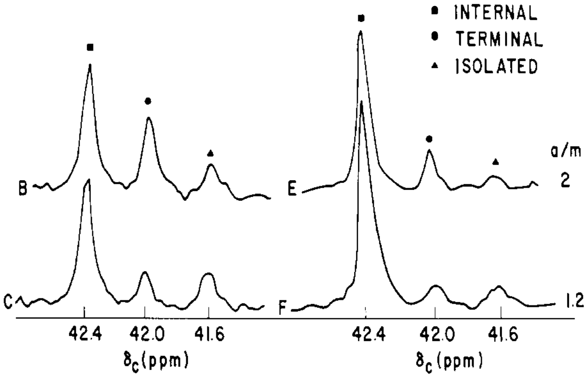


Figure 3. Expansion of the BPA quaternary carbon region of the ^{13}C NMR spectrum for four polymers of identical composition (50 wt % PDMS) but differing in PDMS block length and end-cap ratio: B, $\bar{n}_D$ = 9.3, a/m = 2; C, $\bar{n}_D$ = 9.3, a/m = 1.2; E, $\bar{n}_D$ = 18.4, a/m = 2; F, $\bar{n}_D$ = 18.4, a/m = 1.2.

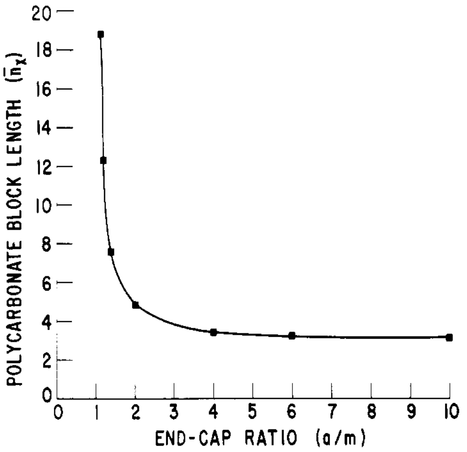


Figure 4. Plot of polycarbonate block length ($\bar{n}_{\mathrm{X}}$) as a function of end-capping ratio for a polymer which is 50 wt % PDMS and has a PDMS block length $\bar{n}_{\mathrm{D}}$ = 9.3. (Courtesy of S. Y. Hobbs.)

in Table I. Two sets of experimental data which were obtained from the same spectrum but different plot widths for the quaternary aliphatic carbon region are presented for each sample in order to show the reproducibility of these measurements. The largest deviation from the calculated polycarbonate block length occurs for the materials prepared with a/m = 1.2. The most likely reason for this is the extreme sensitivity of $\bar{n}_{\mathrm{X}}$ to a/m in this region. As depicted graphically in Figure 4, slight errors in measuring a/m between 1.1 and 1.8 will generate large deviations from the expected $\bar{n}_{\mathrm{X}}$. The deviation of $\bar{n}_{\mathrm{X}}$ (^{13}C) from the expected value in sample C ($\bar{n}_{\mathrm{D}}$ = 9.3 and a/m = 1.2) can be accounted for by assuming an end-cap ratio of 1.47 instead of 1.2. Likewise, sample F would have an average block length of about 22 if the end-cap ratio had actually been 1.4. Variation in composition from 50 wt % silicone also affects $\bar{n}_{\mathrm{X}}$. The value of $\bar{n}_{\mathrm{X}}$ obtained from the ^{13}C NMR spectrum is much closer to the calculated value (for a/m = 4 and 2, samples A, B, D, and E) when the calculation is corrected to account for the actual composition of the polymer as determined by silicon analysis.

The information available from ^{13}C NMR spectroscopy affords a means of monitoring the actual composition of these copolymers, regardless of variations in synthesis or uncertainties in measured quantities. It therefore provides a more direct analysis of these systems for studies of the effects of structural changes on properties. Samples C and D, for example, were designed to differ in average BPAC sequence length by five units (12.3 and 7.0, respectively). By ^{13}C NMR, however, they were found to have the same BPAC block length (~8.5) and thus should have the same domain size according to the physical model of Niznik and LeGrand.[3] A significantly higher amount of the BPA in polymer C is tied up in PDMS–BPA oligomers, and as a result the volume fraction of these domains in C should be smaller than in D. Also, the average PDMS–BPA oligomer in C contains three silicone blocks ($\bar{n}_{\mathrm{D}}$ = 9.3) and two BPA links. Sample D has very few isolated BPA units and therefore the silicone portion of the polymer is largely comprised of chains with the starting siloxane chain length, $\bar{n}_{\mathrm{D}}$ = 18.4. These results are consistent with a higher modulus and tensile strength which was observed for D.

Experimental Section

Polymers. Samples A–F were obtained from Dr. G. E. Niznik and were prepared according to published procedures.[3]

NMR Measurements. The ^{13}C NMR spectra were obtained on a Varian FT-80A NMR spectrometer operating at 20 MHz for ^{13}C. All spectra were acquired with complete proton decoupling and with deuterated solvents for field/frequency control (lock). Samples were doped with ca. 0.1 M tris(acetylacetonato)chromium to shorten the T_1's and suppress the NOE.[4] A gated decoupling sequence and 2-s pulse delay were used to eliminate any residual NOE and allow for complete relaxation of all carbon nuclei. Typical spectral parameters were 4000-Hz spectral width, pulse width corresponding to a 45° flip angle, 1-s acquisition time, and 2-s pulse delay. The 16K data points allowed for 8K output data points in the transformed spectrum. The BPA quaternary aliphatic carbon region of each spectrum was plotted at 57- and 33-Hz plot widths. Quantitative determinations were made by measuring peak areas with a Zeiss MOP-3 image analyzer to give the data shown in Table I. Chemical shifts are reported in ppm relative to Me_4Si with positive values downfield.

Acknowledgment. We thank Drs. D. G. LeGrand and S. Y. Hobbs for very helpful discussions.

References and Notes

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Measurement of the Polymer-Bound Fraction at the Solid–Liquid Interface by Pulsed Nuclear Magnetic Resonance

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ABSTRACT: Pulsed nuclear magnetic resonance (NMR) techniques have been used to estimate the polymer-bound fraction, $\langle p \rangle$, at solid surfaces in both aqueous and nonaqueous dispersions. The measured values are consistent with estimates of the strength of the polymer/substrate interaction energy. Spectra have also been obtained for a terminally anchored polymer.

Introduction

Several experimental techniques now exist for measuring the fraction of segments of an adsorbed polymer that lie in an interfacial plane (trains). These techniques include infrared (IR),[1] microcalorimetry,[2] and electron spin resonance (ESR).[3] Although good agreement has been found between microcalorimetry and IR[2] measurements, the ESR method gives substantially higher values for the number

0024-9297/81/2214-1018$01.25/0