Structural studies of diallyl phthalate–styrene copolymers using nuclear magnetic resonance

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The structures of copolymers of diallyl phthalate and styrene have been investigated using high-field nuclear magnetic resonance (n.m.r.). A method has been developed to measure accurately the amount of each component in the copolymer and to determine the ratio of 'dangling' diallyl phthalate groups to cyclized groups. This ratio is an important parameter in determining the properties of the polymer. Two-dimensional n.m.r. techniques have been used to assign the proton and ^{13}C spectra obtained at 500 and 125.7 MHz respectively. This new method has been used to investigate the dependence of the degree of unsaturation on polymer composition, temperature of polymerization and percentage conversion.

(Keywords: nuclear magnetic resonance; copolymers; diallyl phthalate; styrene; molecular structure)

INTRODUCTION

The polymerization properties of allyl compounds differ markedly from those of vinyl compounds. This has been associated with the possibility of forming relatively stable and unreactive allylic radicals in the former case[1]. As a result of this difference in chemistry, the polymers and copolymers of allylic monomers have a number of uniquely interesting properties[2]. The initial product of a polymerization reaction involving these substances is fusible, soluble in solvents and presumed to have a branched structure. It can be subsequently reacted to give a gel which is an infusible, insoluble space-network polymer[3]. These special properties have led to a large number of commercial applications. The general method of manufacture is to stop the polymerization before the gel point is reached and precipitate the 'prepolymer'. Ideally, this material should have one double bond for each molecule of allyl monomer incorporated, i.e. the remaining unsaturation should be 0.5 of that originally present. In practice this ratio is not usually attained since side reactions, mainly intramolecular cyclization, reduce the degree of unsaturation. Values for the degree of unsaturation in the range 0.25–0.30 are common[4].

The degree of unsaturation depends mainly on competition between unimolecular cyclization reactions and bimolecular propagation reactions with other molecules. It would be anticipated that copolymerization of an allyl monomer with a vinyl comonomer would affect the cyclization reaction. Copolymerization of diallyl phthalate (DAP) with styrene[5,6] is a combination that has achieved some popularity. An important problem in the characterization of these copolymers is the determination of the amount of unsaturation. It has been usual to perform this analysis by iodometric titration and to combine these data with a determination of the total percentage of DAP units using elemental analysis and/or i.r. spectroscopy. It would be very useful to develop an analytical technique to determine simultaneously the ratio of the two comonomers in the polymer and the degree of unsaturation of the allyl component. The present article describes an n.m.r. method developed to carry out this analysis and, for the first time, to characterize diallyl phthalate–styrene copolymers in some detail.

N.m.r. has been used for some 30 years to obtain structural information on polymers[7]. Recently though, there has been considerable expansion of this usage largely because of the development of high-resolution solid-state instruments and the increasing use of more sophisticated multi-pulse experiments in the solution work. The latter area has been reviewed recently by Bovey and Mirau[8]. The use of a number of these techniques will be highlighted in the present report.

EXPERIMENTAL

Preparation of copolymer samples

Polymerization was carried out thermally in glass ampoules. The ampoule, containing the required amounts of DAP and styrene, was degassed twice by the usual freezing and thawing technique under vacuum (10^{-5} hPa) and then sealed. After a measured reaction time the mixture was quenched by immersion in liquid nitrogen. The product was then diluted with chloroform and poured into a large amount of chilled (-10°C) methanol to precipitate the polymer. This precipitation procedure was repeated. After the second precipitation,

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Table 1 Diallyl phthalate–styrene (DAP–Sty) polymers

Sample	DAP content in monomer (mol%)	Temp. of polym. (°C)	Conversion (wt%)	DAP content in copolymer^a (mol%)
20SP20	50	200	9.8	9.7
23SPA1	50	230	16.2	12.0
23SPA4	50	230	35.7	18.0
23SPA5	50	230	51.1	28.0
25SPA1	50	250	11.8	11.1
25SPA2	50	250	22.4	15.3
25SPA4	50	250	41.7	27.5
23SPB1	80	230	5.9	32.6
23SPB3	80	230	14.1	47.0
23SPB5	80	230	37.5	66.0
25SPB1	80	250	6.6	33.5
25SPB2	80	250	11.7	42.5
25SPB5	80	250	47.8	67.5

^{a} Determined from intensity of i.r. CO band

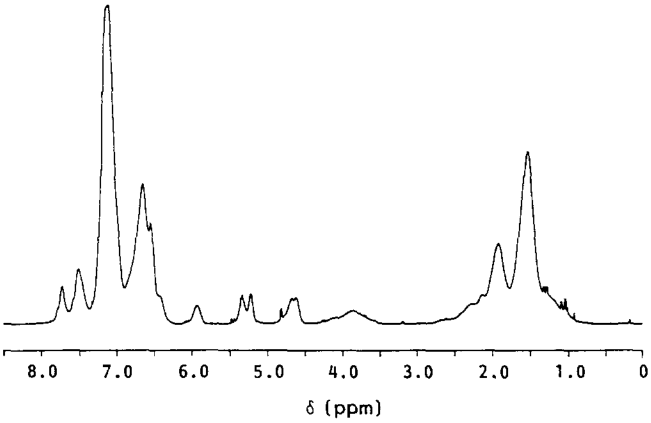

Figure 1 500 MHz ^{1}H spectrum of a copolymer of DAP and styrene (sample 23SPA1). Solvent CCl_4

g.p.c. analyses showed no significant amount of monomer in the final product.

The DAP content in the copolymer was determined by i.r. spectroscopy using the carbonyl band at 1725 cm^{-1} for this purpose. This analytical data will be compared with the n.m.r. data below. A selection of copolymer samples with different DAP contents were selected for the n.m.r. study.

N.m.r. spectroscopy

^{1}H and ^{13}C n.m.r. spectra were obtained in deuteromethylene chloride solution on a Bruker AM500 spectrometer operating at 500 MHz for proton spectra and at 125.72 MHz for carbon-13 spectra. A few samples were run in CCl_4 to resolve a line overlapped by the solvent resonance in $CHDCl_2$. Standard J-modulated spin-sort experiments on the ^{13}C spectra were carried out to distinguish between CH_3, CH_2, CH and quaternary carbons. Assignments of the proton spectrum were verified by means of ^{1}H–^{1}H (COSY) and ^{1}H–^{13}C shift-correlated two-dimensional experiments[9–13]. Essentially these experiments reveal which resonances are coupled to which and enable a complete assignment to be built up from the assignment of a single peak. Both the ^{1}H and ^{13}C chemical shifts are referenced to tetramethylsilane.

RESULTS

A variety of copolymer samples were synthesized, as described in the experimental section. The samples varied in the ratio of monomers in the reaction mixture, in the temperature of polymerization and in the percentage conversion to polymer. Fourteen samples (including one of poly(DAP) itself), chosen to investigate the effect of these parameters on polymer structure, were selected for n.m.r. studies. The synthetic details of these samples are given in *Table 1*. The mole per cent of DAP units was obtained by i.r. spectroscopy. The major n.m.r. technique used was high-resolution ^{1}H spectroscopy carried out at 500 MHz. Relatively few polymer n.m.r. spectra have been obtained at such a high field and the spectrum shown in *Figure 1* illustrates the advantages in terms of enhanced resolution and increased chemical-shift separation. The proton spectrum of poly(DAP) has previously been reported[14] at 100 MHz but the styrene copolymers have not previously been investigated by n.m.r. As is apparent from *Figure 1*, the signals in the proton spectrum are relatively broad but the high field used gives sufficient resolution to allow analysis. To facilitate the assignment process a sample of pure poly(DAP) was prepared and two samples of the copolymer, one with low DAP content and one with high DAP content, were selected for ^{13}C and two-dimensional (2D) n.m.r. analysis.

Generally speaking the ^{13}C spectra show the greater resolution of chemically different nuclei and are therefore better suited for qualitative analysis. An example of such a spectrum is shown in *Figure 2*. This spectrum also illustrates the spin-sort experiment, which differentiates carbons according to whether they are bonded to an odd number or an even number of hydrogen atoms. The proton spectra are more easily obtained and better suited to quantitative analysis. However, taken alone they often pose assignment problems. These problems can be alleviated by obtaining two-dimensional homo-correlation spectra (COSY), an example of which is shown in *Figure 3*. However, in order to complete the assignment it is also desirable to obtain the shift-correlated (^{13}C–^{1}H) 2D spectrum, which provides a link between the known ^{13}C assignments and the unknown ^{1}H assignments. The ^{1}H and ^{13}C assignments resulting from the analysis are given in *Table 2*.

An example of the type of argument used is provided by

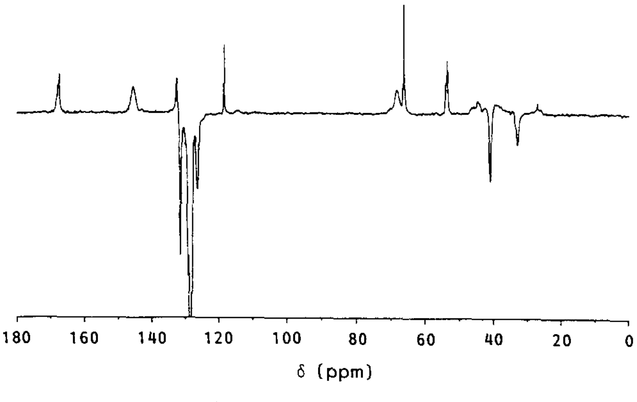

Figure 2 125.7 MHz ^{13}C spectrum of a copolymer of DAP and styrene (sample 25SPB1). Solvent CD_2Cl_2. The spectrum shows the effect of the spin-sort pulse sequence—quaternary carbons and CH_2 appear as positive peaks, CH and CH_3 as negative peaks

a consideration of the assignments of the OCH_2 peaks. If there are both 'dangling' DAP groups and cyclized DAP groups, we would expect three different kinds of OCH_2 groups, two showing coupling to the polymer backbone and one, adjacent to the olefinic group, not showing such coupling (see structure of *Figure 4*). The spin-sort ^{13}C spectrum permitted the assignment of two resonances, a broad signal at 68.4 ppm along with a sharp line at 66.5 ppm, to backbone-bound and dangling OCH_2 groups, respectively. Clearly, the environments of backbone-bound OCH_2 groups derived from either dangling or cyclized DAP molecules are quite similar. This is reflected by the observation of only two resonances for the OCH_2 groups. The information derived from the spin-sort experiments combined with the shift-correlated ^{13}C–^{1}H 2D spectrum provided conclusive evidence for the proton assignments. From the homonuclear COSY spectrum it is apparent that the high-frequency (4.8 ppm) OCH_2 peak is coupled to the olefinic protons and the lower-frequency (3.8–4.2 ppm) peaks are coupled to the backbone protons. It is also significant that the latter resonance is broader than the former as anticipated for nuclei with reduced mobility due to proximity to the relatively rigid backbone of the polymer. These observations determine the assignments of the low- and high-frequency OCH_2 peaks in both the ^{1}H and ^{13}C spectra.

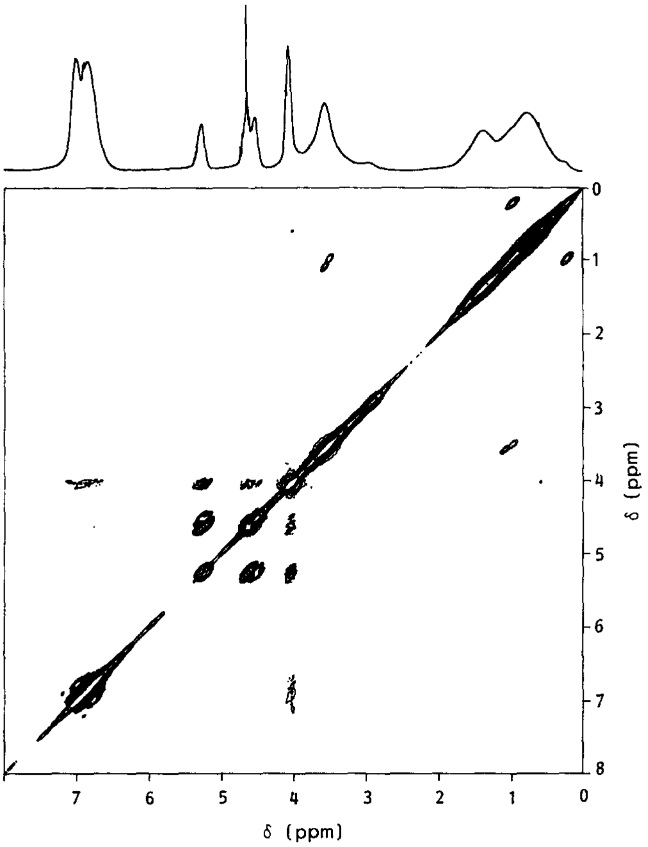

Figure 3 Two-dimensional ^{1}H–^{1}H COSY spectrum of poly(DAP)

Quantitative n.m.r. analysis

Once the assignment of peaks is complete, one may proceed to use the n.m.r. spectra to obtain a quantitative analysis of the number and type of DAP groups in a copolymer sample as well as the styrene content. As

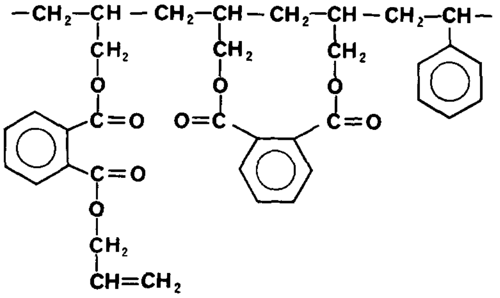

Figure 4 Dangling DAP, cyclized DAP and styrene molecular structures in copolymer

Table 2 N.m.r. assignments

	^{1}H chem. shift	Assignment	^{13}C chem. shift	Assignment
Poly(DAP)	7.53–7.78	Aromatic	167.7	C=O
	5.96	=CH	167.3	C=O
	5.30, 5.32	$=CH_2$	132.5	Quat. arom. C
	4.80	$-OCH_2$ dangling	132.4	=CH
	3.80–4.25	$-OCH_2$ bound to backbone	132.0, 129.7	Arom. CH's
			118.5	$=CH_2$
	1.0–2.5	backbone CH and CH_2	68.4 (broad)	OCH_2, to backbone
			66.5	OCH_2, dangling
			37.0 (broad)	CH_2, backbone
			32.8	CH, backbone
Copolymer	7.54–7.70	Arom. H of DAP	166.8	C=O
	6.45–7.13	Arom. H of Sty	145.8	Quat. C of Sty
	5.94	=CH of DAP	132.5	Quat. C of DAP
			132.5	=CH of DAP
	5.23–5.31	$=CH_2$ of DAP	131.4, 129.2	Arom. CH of DAP
	4.64–4.69	OCH_2 dangling DAP	128.5, 128.1	*o* and *m* C's of Sty
			126.1	*p* C of Sty
	3.5–4.2	OCH_2 bound to backbone	118.5	$=CH_2$ of DAP
			68.4 (broad)	OCH_2 DAP to backbone
	0.9–2.5	CH and CH_2 of backbone	66.5	OCH_2 dangl. DAP
			46.0, 44.2 (broad)	backbone CH_2 Sty
			40.2 (broad)	backbone CH Sty
			37.0 (broad)	backbone CH_2 DAP
			32.3 (broad)	backbone CH DAP

Table 3 N.m.r. analysis of copolymers

Sample	Styrene (mol%)	DAP in copolymer (mol%)	Dangling DAP (mol%)	Cyclized DAP (mol%)	Ratio of dangling to cyclized DAP
20SP20	89.6	10.4	8.0	2.4	3.38
23SPA1	83.9	16.1	11.7	4.4	2.70
23SPA4	78.8	21.2	11.7	9.5	1.24
23SPA5	75.5	24.5	13.0	11.5	1.14
25SPA1	89.5	10.5	8.3	2.2	3.82
25SPA2	81.4	18.6	11.2	7.4	1.51
25SPA4	78.6	21.4	12.2	9.2	1.33
23SPB1	66.5	33.5	22.7	10.8	2.11
23SPB3	52.5	47.5	26.3	21.2	1.24
23SPB5	46.5	53.5	28.4	25.1	1.13
25SPB1	61.8	38.2	26.1	12.1	2.16
25SPB2	57.2	42.8	25.7	17.1	1.50
25SPB5	45.4	54.6	23.9	30.7	0.78
Poly(DAP)	–	100	51.5	48.5	1.06

indicated above, the proton spectrum is best suited to this purpose. The method adopted may be illustrated by reference to a specific example. In a given proton spectrum the area of the olefinic CH (5.9 ppm) resonance was measured at 181 units. This corresponds to one proton of a 'dangling' DAP group. Since there are four OCH$_2$ protons in each such unit the corresponding OCH$_2$ intensity will be (4×181) units. However, the total OCH$_2$ intensity measured for this particular sample was 1061 units. It follows that $1061-(4 \times 181)=337$ units of this intensity must have originated from cyclized DAP. Since each cyclized DAP contains four OCH$_2$ protons, each cyclized DAP proton contributes 84 units of intensity. The ratio 84/181 therefore corresponds to the ratio of cyclized to dangling DAP. Measurement of the total intensity of the backbone CH and CH$_2$ protons yields the ratio of styrene to DAP in the copolymer. Thus in this specific case the area of the total backbone CH and CH$_2$ resonances was 2334 units. We may calculate that 3×181 units of this total was contributed by the dangling DAP and 6×84 units by the cyclized DAP. This leaves 1287 units for the three backbone hydrogens contributed by the styrene, i.e. 429 units per proton. The ratio of styrene units to dangling DAP units is therefore 429/181 in this sample. Measurement of the area of the aromatic proton peaks provides an internal check on the consistency of this analysis. Thus in the present case we may calculate the expected aromatic intensity to be 4×181 units from the dangling DAP, plus 4×84 units from the cyclized DAP, plus 5×429 units from the styrene aromatic protons. This gives a calculated intensity of 3205 units which may be compared with the measured intensity of 3136 units. Analyses along these lines have been performed on 13 samples. The correlation coefficient for the agreement between observed and calculated aromatic intensities for all 13 samples is 0.9973. The results of the n.m.r. analyses are collected in *Table 3*.

DISCUSSION

It has been demonstrated that n.m.r. provides a convenient and accurate method for structural analysis of DAP–styrene copolymers. The analysis for the ratio of the two monomers differs from the data obtained by the more usual i.r. method by, on average, 10%. This is illustrated by comparison of the data for DAP content in *Table 1* (i.r.) with that for the same samples in *Table 3* (n.m.r.). We consider the n.m.r. data to be more reliable since the analysis of the spectra is more complete and there is a direct relationship between n.m.r. signal area and the number of nuclei present. The intensities of i.r. bands must be calibrated individually. In addition to the ratio of the monomer content the n.m.r. method also gives the ratio of dangling DAP to cyclized DAP. This is an important parameter for practical purposes, since for most uses it is necessary to maximize the amount of dangling DAP in the prepolymer and hence the amount of crosslinking in the final product.

The data of *Table 3* illustrate the variation of the structure of DAP–styrene copolymers in terms of three variables—the temperature at which the polymerization was carried out, the relative proportions of the monomers in the polymerizing mixture and the percentage conversion to polymer. Neither the composition of the final product nor the ratio of dangling to cyclized DAP appear to be affected to a significant extent by polymerization temperature. The percentage of DAP in the polymer parallels that in the monomer mixture but is always lower. This result is to be anticipated since allyl compounds always polymerize less readily than vinyl compounds so the initial rate of incorporation of DAP in the copolymer would be expected to be less than that of styrene. Comparing copolymers obtained at initial stages of the polymerization, one can notice that the products from the equimolar styrene/DAP monomer composition have a higher ratio of dangling to cyclized DAP than do those from the styrene/DAP = 20/80 mol% monomer composition. The ratio does, however, depend on the percentage conversion. With increasing conversion, more cyclization takes place. This can be explained mainly by compositional drift resulting from a decreasing amount of the more reactive styrene in the monomer mixture. This trend is obviously undesirable for the commercial polymerization process. However, by introducing the monomers in a continuous fashion, it is possible to diminish the compositional drift.

These results demonstrate that high-resolution n.m.r. provides a rapid and reliable approach to solving structural problems in polymer chemistry. The use of the more sophisticated two-dimensional experiments is likely to become increasingly common as predicted by Bovey and Mirau[8] in their recent review.

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