Unsaturated polyesters based on terephthalic acid:
4. Sequence distribution of crosslinks in styrene cured resins

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The sequence distribution of the styrene crosslinks in a cured polyester formed from propylene glycol, terephthalic acid and maleic anhydride has been studied by ^{13}C nuclear magnetic resonance and infra-red spectroscopy. The n.m.r. method involved the degradation of the crosslinked polyester into a copolymer of styrene and fumaric acid and the interpretation of the peaks in the ^{13}C spectrum, which arise from the quaternary phenyl carbon atoms in sequences of styrene units, by considering the ^{13}C spectra of copolymer standards of styrene and diethyl fumarate. The crosslinking process was monitored directly by infra-red spectroscopy, and the distribution of sequence lengths of styrene units was then estimated by considering that crosslinking may be interpreted by a statistical treatment of copolymerization. Values of mol fractions of styrene units in sequences of monads, diads and triads determined by ^{13}C n.m.r. and infra-red spectroscopy were in fair agreement.

INTRODUCTION

A polyester resin is produced by dissolving in styrene an unsaturated polyester prepared from saturated and unsaturated acids, or their anhydrides, and a glycol and curing by radical copolymerization. The properties of the cured resin are influenced by the degree of crosslinking and the length of the crosslinking bridges between the polyester chains[1]. The average number of homopolymerized styrene units constituting these crosslinks has been determined from an examination of the degradation product resulting from the hydrolysis of the ester units in the cured polyester resin. Funke and co-workers[2–4] subjected the degradation product to characterization by infra-red spectroscopy which was also employed by Learmonth and Pritchard[5] who suggested an average of between 1 and 5 styrene units per crosslink in their resins. The styrene units in the degradation products have also been characterized by Laser Raman spectroscopy[6], elemental analysis[7] and isotopic labelling[8].

Nuclear magnetic resonance (n.m.r.) spectroscopy has proved to be a useful technique for copolymer characterization, and extensive details can be found in the book by Bovey[9]. The use of ^{1}H n.m.r. for estimating the styrene sequence length originated from the studies of emulsion copolymers of styrene and butadiene by Bovey and co-workers[10]. Further studies of ^{1}H spectra by Mochel[11,12] suggested that sequences consisting of two or three styrene units in styrene–butadiene copolymers could be determined by a computer method involving the resolution of the overlapping n.m.r. peaks due to aromatic protons. The use of ^{13}C n.m.r. is much more attractive than ^{1}H n.m.r. for copolymer characterization because of the direct observation of backbone nuclei, the broad range of chemical shifts, and the simplicity of ^{1}H decoupled spectra. Comonomer sequence distributions expressed as connecting diads and triads may be determined. The analysis of styrene copolymers depends on the sensitivity of the quaternary phenyl carbon to both structural and configurational differences. Published spectra of pure polystyrene show the region due to the quaternary phenyl carbon (around 145 ppm downfield from TMS) to consist of three peaks corresponding to the isotactic, syndiotactic and heterotactic configurations[13]. Since these peaks cover a range of only 2.5 ppm while multiplicities due to structural effects (comonomer distribution) cover ~8 ppm, it is assumed that the gross features of the quaternary phenyl carbon absorption region are due to different structural units with configurational differences causing broadening of the peaks. Schaefer[14] used ^{13}C n.m.r. to study the monomer distribution in acrylonitrile–styrene copolymers, whilst Buchak and Ramey[15] used the same technique to determine the styrene sequence distribution in low molecular weight styrene–maleic anhydride copolymers. The relative concentrations of the styrene triads, diads as well as monads, may be calculated from the areas under the peaks due to the phenyl quaternary carbons.

In previous papers, the characterization of poly(propylene terephthalate) prepolymer has been reported[16–18]. An unsaturated polyester is produced from the reaction between this prepolymer and maleic anhyd-

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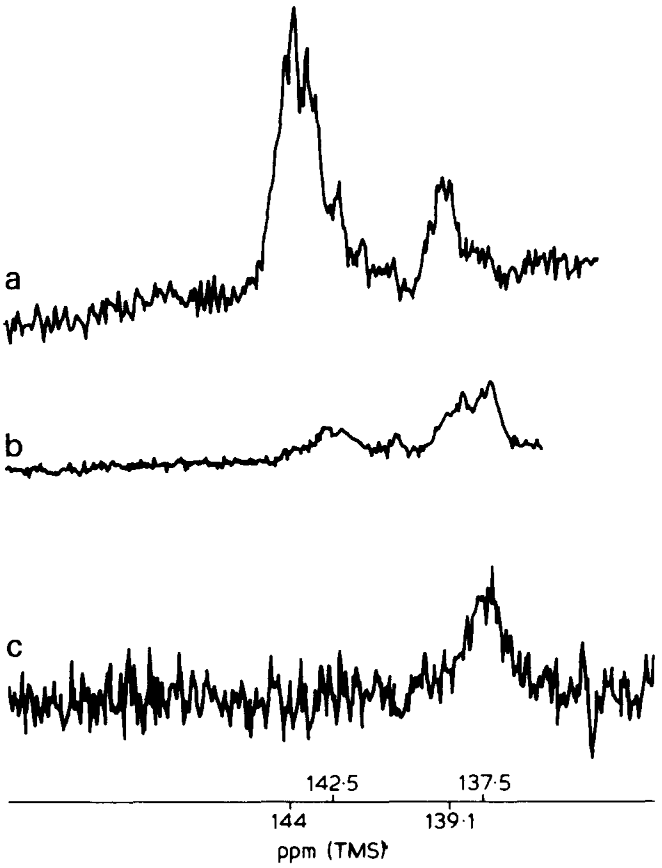


Figure 1 Proton decoupled natural abundance ^{13}C n.m.r. spectra of copolymer standards of styrene and diethyl fumarate. a, 90% styrene in feed; b, 57% styrene in feed; c, 10% styrene in feed

ride and is crosslinked by curing with styrene. In this paper, the determination of the sequence distribution of the styrene crosslinks by two methods is described. In the first, the crosslinked polyester was degraded to a copolymer of styrene and fumaric acid, and the ^{13}C absorptions of the quaternary carbon atom in styrene were assigned to sequences of styrene units by considering the ^{13}C spectra of copolymer standards of styrene and diethyl fumarate. In the second method, the whole crosslinking process was followed by infra-red spectroscopy and the styrene sequences were determined from the statistical treatment of changes in spectra occurring during curing.

EXPERIMENTAL

^{13}C n.m.r. spectroscopy

The T500 Impolex resin (Imperial Chemical Industries Limited) consisted of an unsaturated polyester, prepared from propylene glycol (3.3 mol), terephthalic acid (1 mol), and maleic anhydride (2 mol), dissolved in styrene (50%, w/w). ^{1}H n.m.r. analysis of the unsaturated polyester showed that 95% of the original maleate was converted into unsaturated fumarate. The resin was cured with 1% (w/w) methyl ethyl ketone peroxide (Laporte SD2) and 2% (w/w) cobalt octoate solution (Noradel NL 49/ST). The curing was allowed to proceed for 5 h at room temperature (293K), and then at 333K (2 h), 353K (1 h), and finally 393K (1 h). The cured resin was saponified with potassium hydroxide in benzyl alcohol according to the procedure described by Funke and co-workers[2-4]. The resulting poly(carboxylic acid) was esterified with diazomethane.

The copolymer standards of styrene and diethyl fumerate were prepared at 333K by radical copolymerization of bulk monomers with azobisisobutyronitrile as initiator in an atmosphere of nitrogen for 5 h. Under these conditions the monomer reactivity ratios of styrene and diethyl fumarate are 0.3 and 0.07 respectively[19]. Three copolymers were selected for the ^{13}C n.m.r. standardization. The first was synthesized from a feed containing 90% styrene and thus was expected to contain long styrene sequences. The second was synthesized from 57% styrene, which should give short styrene sequences with monads being the most prevalent sequence. Finally, the third standard was obtained from a feed of 10% styrene so that almost all the styrene was present as monads, and the copolymer may be regarded as having an alternating structure. The mol fraction of styrene in this copolymer was found to be equal to 0.45 by ^{1}H n.m.r. spectroscopy.

The ^{13}C spectra of the esterified degradation product and the copolymer standards were recorded on a Varian XL100–15 Fourier Transform n.m.r. spectrometer operating at 25.2 MHz. Proton–noise decoupling was used throughout and a standard VFT–100X Fourier transform system. The samples (20%, w/w) dissolved in dimethyl sulphoxide (d_6) were examined in n.m.r. tubes (12 mm OD) at 403K. The solvent also provided a deuterium signal for field/frequency stabilization. A full spectrum (200 ppm) was obtained with the following spectrometer conditions: spectral width = 5 000 Hz, acquisition time = 0.8 s, pulse width = 90 μs, points Fourier transformed = 8 000, number of transients = 40 000. Expanded spectra were obtained under the following conditions: spectral width = 2500 Hz, acquisition time = 1 s.

Infra-red spectroscopy

T500 Impolex resin (5 g) was mixed with methyl ethyl ketone peroxide catalyst (0.5 g) and cobalt octoate accelerator (0.05 g). A small quantity of this resin was applied to a NaCl infra-red disc which was topped by a second disc. Both discs, separated by a PTFE spacer (0.025 mm), were clamped in position and were exposed to infra-red radiation for various time intervals. The quantity of resin was sufficient to fill the available space between the discs and to allow a well defined spectrum to be obtained. Spectra were recorded at different time intervals on the same chart.

RESULTS AND DISCUSSION

^{13}C n.m.r. of copolymer standards

The downfield absorption region of the quaternary phenyl carbon in each of the copolymers of styrene and diethyl fumarate is shown in *Figure 1*. Whereas the spectrum of styrene homopolymer in $CDCL_3$ in *Figure 2* exhibits a single absorption in this region at 145.3 ppm, two of the standards have this absorption split into at least three peaks. The difference between the chemical shifts of 144 ppm in *Figure 1a* and 145.3 ppm in *Figure 2* for long sequences of styrene units arises because the spectra of the copolymer standards and polystyrene were taken with different solvents.

In order to assign these peaks to specific styrene units along the copolymer backbone, we define a monad sequence (I), diad sequence (II), and *n*-ad sequence (III), where $n > 2$, by the structures

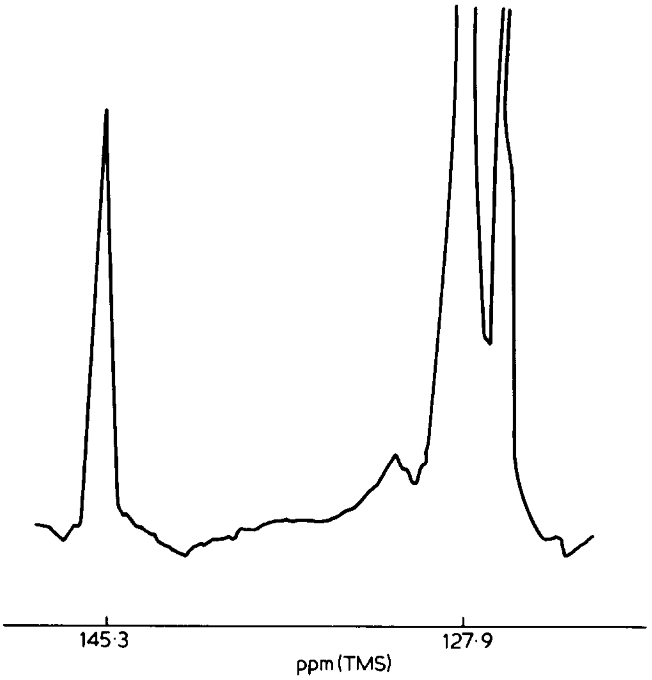
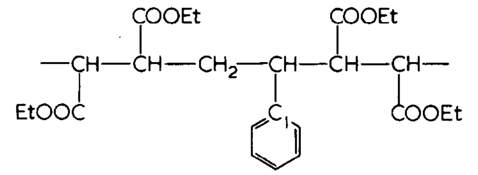
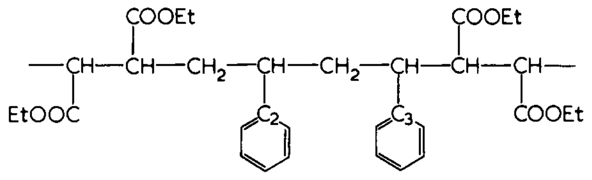


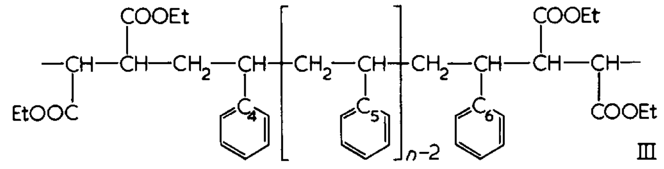
Figure 2 ^{13}C n.m.r. spectrum of polystyrene in $CDCl_3$



I



II



III

Isomeric forms in I, II and III have been ignored because they result in trivial chemical shifts (see Introduction). The quaternary phenyl carbon C_1 in I constitutes a structural unit on its own since it is flanked by 2 fumarate units. However, the C_2 and C_4 carbons in II and III will be structurally and magnetically similar, as will the C_3 and C_6 carbons. Both sets of quaternary phenyl carbons have a styrene unit on one side and a fumarate unit on the other, the only difference being the mode of attachment of the last styrene unit to the fumarate unit. Finally, the C_5 carbon in III constitutes a structural unit on its own since it is flanked by 2 styrene units. This approach represents an extension of the assignments reported by Schaefer[14] and Buchak and Ramey[15] who reported ^{13}C spectra of styrene copolymers. They interpreted the splitting of the peaks due to the quaternary phenyl carbons in terms of the environment of a central styrene unit in a triad formed from styrene and the comonomer. A summary of our assignment of the peaks in the spectra in *Figure 1* to sequences of styrene units is presented in *Table 1*.

The quantitative analysis of the tabulated assignments is based on two facts. First, the area under the absorption peak is proportional to the number (mol) of species responsible for the absorption, and second, because of the resolving power of the spectrometer the triad peaks overlap with the peaks of higher order sequences. If we assume that a copolymer consists of a mol of $-C_1-$ monads, b mol of $-C_2-C_3-$diads and c mol of $-C_4-(C_5)_{n'}-C_6-$ n-ads, where $n' = n-2$, then the number of mol of each styrene type will be: a mol of styrene (C_1), b mol of styrene (C_2) and styrene (C_3), c mol of styrene (C_4) and styrene (C_6), and $(n-2)$ c mol of styrene (C_5). It follows that the peak area at 137.5 ppm is equivalent to a mol of monads, the one at 139.1 ppm to b mol of diads plus c mol of n-ads, the one at 142.5 ppm to b mol of diads plus c mol of n-ads again and therefore its area should be equal to the previous peak area. Finally, the peak at 144 ppm is equivalent to $(n-2)$ c mol of n-ads ($n > 2$). Accordingly, the number of monads a can be easily determined since they give rise to a well defined peak. The values of b and c can be estimated if $n = 3$, otherwise only a tentative guess of their values can be reached.

The application of this anslysis may be demonstrated for the spectrum in *Figure 1* of the copolymer prepared from a monomer feed consisting of 90% styrene. The two major peaks centred at chemical shifts of 139.1 and 143.5 ppm yield peak areas of 2.56 cm^2, equivalent to $b+c$, and 9.72 cm^2, equivalent to $b+c+(n-2)c$, since the latter area results from two overlapping peaks centred at 142.5 and 144 ppm. Consequently, the area of the peak at 144 ppm, equivalent to $(n-2)c$, is 7.16 cm^2. The magnitude of b may be determined from

$$[S - C'/(n-2)] > 0 \qquad (1)$$

where S is assumed to be the area corresponding to the sum $b+c$ and C' the area corresponding to $(n-2)c$. The spectrum assignment is limited to $n=3$ which together with $S = 2.56$ cm^2 and $C' = 7.16$ cm^2 suggests that b calculated from equation 1 is negative which is clearly not possible. For the copolymer under consideration diads of styrene units will be absent. Alternatively, if b is assumed to be zero, then the average value of n is 4.8. We may conclude for the results described in this paper that, when relation (1) is not obeyed with $n = 3$, then the copolymer does not contain diads of styrene units which of course implies that peaks corresponding to monads are absent. Furthermore, if relation (1) is obeyed with $n = 3$, then it may be assumed that sequences of styrene units of higher order than triads are absent. These observations result from the limited resolution of the resonances from the quaternary carbon of the styrene units under the conditions used for the ^{13}C n.m.r. experiment.

Table 1 Assignment ^{13}C n.m.r. peaks to sequences of styrene units

Quaternary phenyl carbon	Sequence	Chemical shift (ppm)
C_1	Monad	137.5
$C_3 + C_6$	Diad + n-ad	139.1
$C_2 + C_4$	Diad + n-ad	142.5
C_5	n-ad	144.0

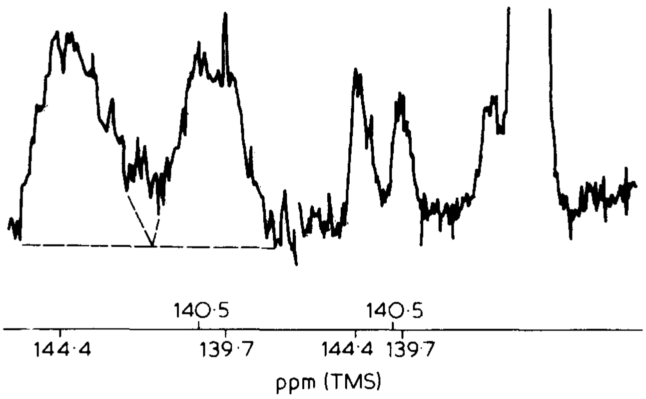


Figure 3 ^{13}C n.m.r. spectrum, and expanded spectrum, of the esterified hydrolysis products from the degradation of T500 cured resin

Table 2 Mol fractions of sequence lengths of styrene units

Technique	Monads	Diads	Triads
^{13}C n.m.r.	0.42	0.25	0.33
Infra-red	0.48	0.30	0.14

^{13}C n.m.r. of the hydrolysis products

The spectrum of the esterified degradation product (a copolymer of styrene and fumaric acid) resulting from the cured T500 Impolex resin is shown in *Figure 3*. Comparison with the spectra for the copolymer standards suggests that the splitting of the C_1 phenyl carbon absorption region is not as good as the resolution of the peaks in *Figure 1*. Initially, the spectra of the standards were recorded at room temperature and they displayed a splitting pattern similar to that of the hydrolysates. However, whilst the spectra of the standards recorded at elevated temperature 403K showed a fine resolution, those of the hydrolysates remained unaffected; this might reduce the accuracy of the numerical results without, however, making the analysis an impossible task.

The phenyl quaternary carbon of the hydrolysate results in two broad resonance peaks centred at 140.0 ppm and 144.4 ppm. The broad peak at 140.0 ppm may be subdivided into a peak centred at 139.7 ppm and caused by monads of styrene and into a peak centred at 140.5 ppm, with an area 6.2 cm^2, caused by C_3 and C_6 carbons of diads and *n*-ads respectively. No attempt was made to resolve the peak at 144 ppm, its area being equal to 9.7 cm^2. These results may be interpreted in terms of relation (1) which is obeyed for values of $n \geqslant 3$ with $S = 6.2$ cm^2 and $C' = 3.5$ cm^2. If we assume $n = 3$, as discussed previously, the number of diads is equivalent to 2.7 cm^2 and the monads are equivalent to the area of the first peak, i.e. 4.4 cm^2. Therefore, the styrene triads, diads and monads constituting the cross-linking bridges in a cured T500 Impolex resin are in the ratio 3.5:2.7:4.4, giving the corresponding fractions shown in *Table 2*. This result can be interpreted in two different ways. It can either be accepted as it is, i.e. that longer sequences than triads are not formed during crosslinking and therefore the reaction does not proceed statistically, or that the copolymerization does proceed statistically and that sequences of more than three styrene units are formed but are not detected. It may be concluded that the sequences of styrene units constituting the crosslinked network of a T500 Impolex resin consist of less than 50% monads, about 25% of diads, and the rest are triads, tetrads, etc. in decreasing population.

From an experimental point of view, this ^{13}C method can be used to follow the distribution of the styrene sequences at various stages of the crosslinking process, after hydrolyzing samples taken from a resin during its curing cycle and esterifying the resulting copolymers. Furthermore, the effect of structural variables such as the distribution of the double bonds along the polyester chain as well as the effect of fillers and curing conditions on the sequence distribution of the crosslinks can also be studied by this method. The only drawback is the poor resolution of the resonance peaks corresponding to styrene *n*-ads ($n > 2$).

Infra-red spectroscopy

The use of infra-red spectroscopy for monitoring the crosslinking of unsaturated polyesters has been documented[20,21]. It consists of following the disappearance of infra-red absorption bands specific to the fumarate and styrene double bonds. A typical spectrum is shown in *Figure 4*. The bands due to styrene double bonds which do not overlap with any other band are the ones at 907 cm^{-1} ($=CH_2$ wag) and at 1629 cm^{-1} ($C=C$ stretch). The fumarate double bonds, alternatively, have only one characteristic non-overlapping absorption in the spectrum at 1640 cm^{-1} ($C=C$ stretch). For the quantitative purposes of the present work consideration will be given to the styrene and fumarate absorptions at 1629 cm^{-1} and 1640 cm^{-1} respectively, to which will be assigned a single common base line. The changes in band intensities with time are interpreted in terms of the absorbance difference between the base line and the peak of the absorption band, so that the consumption of double bonds can be calculated provided Beer's law is assumed to be applicable and the initial concentration of monomer is known. For a given band, the ratio of the absorbance after a curing time to the absorbance at the start of the crosslinking reaction gives directly the ratio of monomer present at the corresponding times. The relative changes in double bond

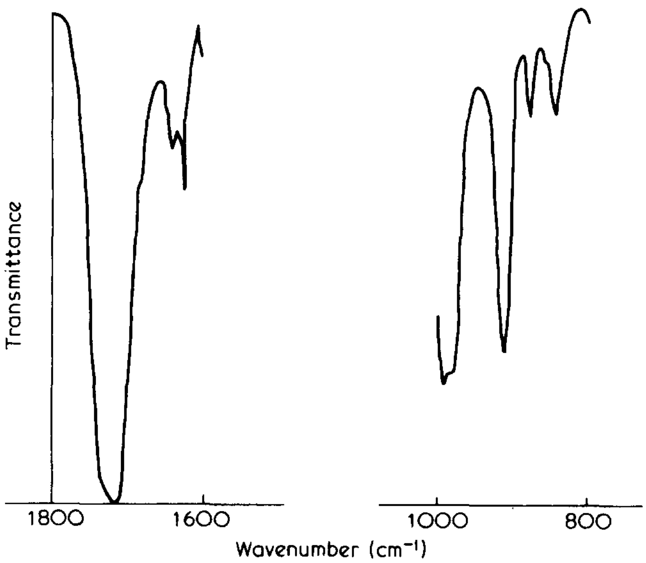


Figure 4 Infra-red spectrum taken after 4 min during the cross-linking of T500 resin

Table 3 Monomer consumption by infra-red spectroscopy during curing of a T500 resin

	Fumarate (%)				Styrene (%)			
	With respect to feed		With respect to amount left free from previous stage		With respect to feed		With respect to amount left free from previous stage	
Time (h)	Free	Reacted	Free	Reacted	Free	Reacted	Free	Reacted
0.07	100	0	100	0	100	0	100	0
1.75	65.5	34.5	65.5	34.5	72.1	27.9	72.1	27.9
2.83	44.8	55.2	68.4	31.6	54.3	45.7	75.4	24.6
4.00	34.5	65.5	76.9	23.1	44.7	55.8	81.3	18.7
15.00	13.8	86.2	40	60	13.7	86.3	31.0	69
+20.00 at 353K	5.5	94.5	40	60	1.0	99.0	7.4	92.4

Table 4 Molar concentration by infra-red spectroscopy of monomers in feed and monomer units in copolymer network at various stages of the crosslinking process

	Fumarate/Styrene content			
	Feed		Copolymer network	
Time (h)	Mol	Mol fraction	Mol	Mol fraction
0.07	2:2.95	0.4:0.6	–	–
1.75	1.31:2.13	0.38:0.62	0.69:0.82	0.46:0.54
2.83	0.90:1.61	0.36:0.64	0.41:0.52	0.44:0.56
4.00	0.69:1.31	0.35:0.65	0.21:0.30	0.41:0.59
15.00	0.28:0.41	0.41:0.59	0.41:0.90	0.31:0.69
+20.00 at 353K	0.110:0.03	0.79:0.21	0.17:0.38	0.31:0.69

consumption and feed calculated from absorbance values are shown in *Table 3*. These results can be easily translated into molar concentrations of the monomers, since a T500 Impolex resin is prepared from 1 mol of terephthalic acid, 3.3 mol of propylene glycol, 2 mol of maleic anhydride and 50% by weight of styrene. Therefore, in terms of unsaturated monomers, the resin contains 2 mol of maleic anhydride and 2.95 mol of styrene (mol fraction 0.4:0.6). The molar concentrations of unconverted monomers and monomer units incorporated into copolymer are given in *Table 4*.

The relation between infra-red absorption and the statistical treatment of sequence length distribution has been considered for copolymers of styrene and methyl acrylate[22] and for copolymers of styrene and acrylonitrile[23]. The mol fractions given in *Table 4* may be used in the determination of the fractions of sequence lengths of styrene units according to the statistical treatment presented by Bovey[24]. The probability $P_{m,n}$ that a sequence of monomer units m chosen at random from a copolymer chain will contain n and only n units of a monomer m, e.g. styrene in our copolymers, is given by the following equation

$$P_{m,n} = p^{(n-1)}(-p) \qquad (2)$$

where p is the probability that monomer m will add to a growing chain ending in m. The value of p is evaluated from

$$p = r_1 f_1/(1 - f_1 + r_1 f_1) \qquad (3)$$

where r_1 is the monomer reactivity ratio of one monomer and f_1 is the mol fraction of the monomer 1 in the feed. In our experiments symbol 1 will represent styrene which has $r_1 = 0.3$ in radical copolymerization with diethyl fumarate. The treatment of Bovey[24] gives the mol fraction $F_{m,n}$ of m monomer units in sequences having a length exactly n, as follows:

$$F_{m,n} = n\, p^{(n-1)}(1-p)^2 \qquad (4)$$

It is observed in *Table 4* that apart from the end of the curing reaction there is little change in the monomer feed ratio as a function of time. The copolymerization of the unsaturated polyester, from maleic anhydride (2 mol), with styrene (2.95 mol) is close to the azeotropic composition for styrene ($r_1 = 0.3$) and diethyl fumarate ($r_2 = 0.07$). The value of p was evaluated from equation (3) taking $f_1 = 0.6$, and the mol fractions in *Table 2* were then evaluated with equation (4). Fair agreement with the ^{13}C n.m.r. data is observed. An alternative view is to regard the crosslinking process as a series of independent copolymerization reactions at each time, in order to calculate from the mol fractions of units in the network the monomer feed composition responsible for producing the copolymer composition at each time. From the copolymer composition equation, values of the monomer feed composition are calculated with the values of copolymer composition in *Table 4*, r_1 and r_2. These values for f_1 may be used with equations (3) and (4) to estimate the fractions of the various sequence lengths of styrene units formed at each stage of the copolymerization. The results are presented graphically in *Figure 5*, suggesting that the concentrations of styrene diads and triads increase with time, whereas the concentration of monads decreases.

The accuracy of the infra-red method for determining sequence lengths should be considered. From an experimental viewpoint, the crosslinking process is studied with a very thin film of resin which may cure differently from bulk samples because of temperature variations due to the transfer of heat evolved during copolymerization. From a theoretical standpoint, copolymer composition is calculated from the infra-red data for monomer consumption by a statistical treatment which assumes that monomer reactivity ratios defined in standard copolymerizations are also applicable in the hardening of the polyester network. It has been reported that aggregation behaviour, and the placement of fumarate units in branched and crosslinked chains which may be regarded as an aggregation process, may influence copolymerization behaviour[25]. Furthermore, the dependence of monomer reactivity ratios on temperature has been reported,[26] and

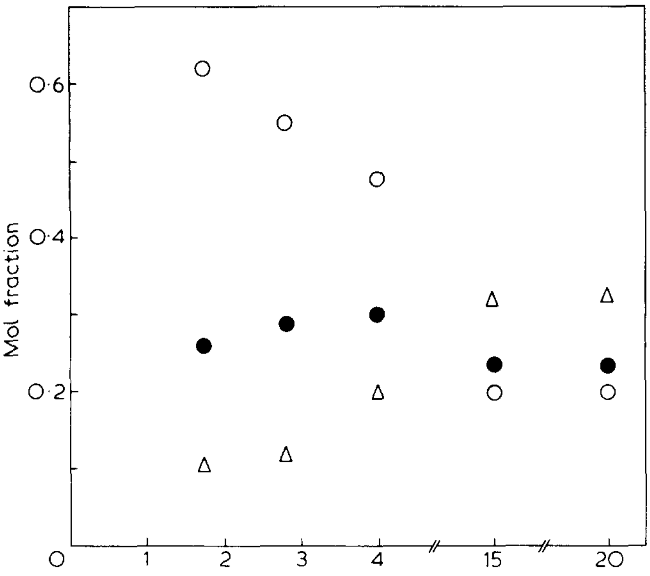


Figure 5 Variation of mol fractions of sequence lengths of styrene units during curing of T500 resin: ○, monads; ●, diads; △, triads

we have neglected this dependence although it is likely that temperature variations may be pronounced during the early stages of the crosslinking reaction. In spite of these deficiencies which appear at first sight to indicate that the infra-red method for determining sequence lengths would be of doubtful accuracy, the data in *Table 4* do suggest that during the first 15 h of crosslinking the reaction between the fumarate in the polyester and styrene proceeds almost as predicted for a copolymerization of diethyl fumarate and styrene close to the azeotropic composition. It is not surprising to find that after this period, the free styrene, owing to the increased mobility relative to the fumarate which is already part of a rigid crosslinked network, is consumed faster and probably gives rise to long styrene sequences. Therefore, in the later stages of the crosslinking process, the simple statistical treatment fails to describe the course of the reaction.

CONCLUSIONS

Peaks due to resonances in ^{13}C n.m.r. from quaternary phenyl carbon atoms in styrene units in unsaturated polyesters have been assigned to styrene units in monad, diad, and *n*-ad sequences, where the *n*-ad sequences may be either triads only or triads plus longer sequences. The sequence distribution of crosslinks in styrene cured unsaturated polyesters may be determined by this ^{13}C n.m.r. procedure, so that the formation of crosslinks during the curing process may be followed. Infra-red spectroscopy is a more practical but less accurate alternative in following the crosslinking process since it involves the use of a statistical treatment which regards the curing reaction as a standard free radical copolymerization of two monomers.

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REFERENCES

1 Parkyn B., Lamb, F. and Clifton, B. V. 'Polyesters: Unsaturated Polyesters and Polyester Plasticisers', Iliffe, London, vol. 2, 1967
2 Funke, W., Gebhardt, W., Roth, H. and Hamann, K. *Makromol. Chem.* 1958, **28**, 17
3 Gilch, H., Funke, W. and Hamann, K. *Makromol. Chem.* 1959, **31**, 93
4 Funke, W., Hamann, K. and Gilch, H. *Angew Chem* 1959, **72**, 596
5 Learmonth, G. S. and Pritchard, G. *SPE J.* 1967, **23**(**12**), 46, 59
6 Koenig, J. L. *J. Polym. Sci.* (*A2*) 1972, **10**, 721
7 Hayes, B. T., Read, W. J. and Vaughan, L. H. *Chem. Ind.* 1957, 1164
8 Ghanem, N. A. *Makromol. Chem.* 1960, **36**, 109
9 Bovey, F. A. 'High Resolution NMR of Macromolecules', Academic Press, New York, 1972
10 Bovey, F. A., Tiers, G. V. D. and Filipovich, G. *J. Polym. Sci.* 1959, **38**, 73
11 Mochel, V. D. *Rubber Chem. Technol.* 1967, **40**, 1200
12 Mochel, V. D. *Macromolecules* 1969, **2**, 537
13 Johnson, L. F., Heatley, F. and Bovey, F. A. *Macromolecules* 1970, **3**, 175
14 Schaefer, J. *Macromolecules* 1971, **4**, 107
15 Buchak, B. E. and Ramey, K. C. *J. Polymer Sci.* (*Polym. Lett. Edn.*) 1976, **14**, 401
16 Birley, A. W., Kyriacos, D. and Dawkins, J. V. *Polymer* 1978, **19**, 1290
17 Birley, A. W., Dawkins, J. V. and Kyriacos, D. *Polymer* 1978, **19**, 1433
18 Birley, A. W., Dawkins, J. V. and Kyriacos, D. *Polymer* 1980, **21**, 632
19 Mayo, F. R. and Walling, C. *Chem. Rev.* 1950, **46**, 191
20 Alekseyeva, I. A. and Spasskii, S. S. *Vysokomol. Soedin* 1960, **2**, 1645
21 Learmonth, G. S. and Pritchard G. *Br. Polym. J.* 1969, **1**, 88
22 Kamiyama, F. and Matsuda, H. *J. Phys. Chem.* 1967, **71**, 4153
23 Naobumi, O. and Koichi, M. *Bunseki Kagaku* 1974, **23**, 798
24 Bovey, F. A. *J. Polym. Sci.* 1962, **62**, 197
25 Bulatov, M. A. and Spasski, S. S. *Polym. Sci. USSR* 1972, **14**, 673
26 Lewis, F. M., Walling, C., Cummings, W., Briggs, E. R. and Mayo, F. R. *J. Am. Chem. Soc.* 1948, **70**, 1519