Mechanisms of the bulk copolyesterification of azelaic acid, o-phthalic anhydride and trimethylolpropane studied by $^{13}$C nuclear magnetic resonance

R. Petiaud, H. Waton and Q. T. Pham*
CNRS, Service Central d'Analyse, BP 22, 69390 Vernaison, France

and H. Coyard
Société Française Hoechst, Centre de Recherches et d'Applications, 48 Avenue Gaston Monmousseau, 93240 Stains, France
(Received 21 October 1991; revised 18 February 1992; accepted 2 March 1992)

Polyesterifications in bulk of trimethylolpropane (T) with azelaic acid (Z) and o-phthalic anhydride (P) and copolyesterification of a (Z+P+T) ternary mixture have been studied by $^{13}$C nuclear magnetic resonance (n.m.r.) before and after gelation. It has been found that Z is more able than P to give covalent gels. $^{13}$C n.m.r. allows quantitative determinations of the conversions of acid functions of Z and P and alcohol functions of T as well as the distributions of monoester and diester of P and those of free, mono-, di- and triesterified T. In all cases, the actual critical conversions are larger than the theoretical ones calculated due to the Flory-Stockmeyer statistics because (i) 3–5% of free T and P are trapped and (ii) the two acid functions of P or Z and the three alcohol functions of T do not have the same reactivities. For the ternary system, four types of T triesters have been identified and quantitatively determined, and finally, reticulation should only occur if more than one-third of T are triesterified. In the copolyesterification in bulk of the (0.5Z + 0.5P + 0.8T) mixture, the distributions of Z and P on the mono-, di- and triesterified T follow Bernoullian statistics.

(Keywords: copolysters; nuclear magnetic resonance spectroscopy; polyesterification; azelaic acid; o-phthalic anhydride; trimethylolpropane; gelation)

INTRODUCTION

Copolysters form a very important class of industrial materials but the mechanisms of the polyesterification, especially with the presence of a trifunctional reagent, are not widely known. Moreover, in industrial synthetises, because of the toxicity of most of the organic solvents, polyesterifications are exclusively performed in bulk at high temperature (> 160°C). In the present case, even at low conversion, trimethylolpropane gives microgels, thus the conversions of acid and alcohol groups can be precisely determined neither by chemical analysis nor by $^1$H n.m.r. Fortunately, these copolysters give well swollen homogeneous gels in most organic deuterated solvents and allow reproducible quantitative determinations by liquid $^{13}$C n.m.r. as has been achieved previously in our laboratory with gelled polybutadiene-urethanes.

Though many polyols—like glycerol, trimethylol-ethane, trimethylolpropane and pentaerythritol—have been utilized, there are no known quantitative studies relating to these polyols in polyesterifications or copolyesterifications.

The present work deals with the $^{13}$C n.m.r. study of the mechanisms of the bulk copolyesterification of the (azelaic acid + o-phthalic anhydride + trimethylolpropane) ternary system. The different types of ester groups have been identified and quantitatively determined. Our attention has been specially focused on the critical conversions and on the nature and the proportions of the mixed triesters of trimethylolpropane—the potential branch points—the identification of which has been aided by statistical methods.

EXPERIMENTAL

Reagents

Trimethylolpropane (T), azelaic acid (Z) and o-phthalic anhydride (P) are commercial powders. Some 3–4 mol% of o-phthalic anhydride (P') were found in P. The $^{13}$C chemical shifts of T, Z, P and P' are reported in Table 1.

* To whom correspondence should be addressed

© 1992 Butterworth-Heinemann Ltd.

5056 POLYMER, 1992, Volume 33, Number 23
**RESULTS AND DISCUSSION**

The three alcohol (aaa) groups of trimethylolpropane (T) become more and more hindered as they are successively esterified (aae, aee and eee) by the acid functions of azelaic acid (Z) or o-phthalic anhydride (P). Consequently, all the peak widths at half-height of T were found to increase with increasing degrees of esterification (from aaa to eee). Besides, in terms of $^{13}$C n.m.r., the chemical shifts of all the carbons of T depend on the nature and the number of esters and/or hydroxyl groups. With a view to facilitate the assignments of all the $^{13}$C resonances of the three-component copolyester (0.5Z+0.5P+0.8T), the polyesterryfications of four binary mixtures (1Z+1.15T), (1Z+1T), (1Z+0.8T) and (1P+0.8T) have been studied first.

**BULK POLYESTERIFICATION OF BINARY SYSTEMS**

Bulk polyesterryfications of (1Z+1.15T) and (1Z+1T)

A typical $^{13}$C n.m.r. spectrum of poly(trimethylolpropane azelaate) (poly-TZ, see Scheme 1) dissolved in DMSO-d$_6$ is shown in Figure 1. The assignment of the complex resonances of the different esterified trimethylolpropanes has been performed using T acetate models. With azelaic acid, because of the long methylene chain, the COOHs of diacid (AA) and monoacid monoester (AE) have the same chemical shift (174.6 ppm). Thus, only the global conversions of acid groups (C(Z) %) may be calculated using the relative intensities of CO acid (COOH, 174.6 ppm) and CO esters (COOCH$_2$, three peaks in the 171.5–173.5 ppm region) (see Figure 3):

$$C(Z) \% = 100 \times \frac{(COOCH_2)}{(COOH)+(COOCH_2)}$$  

Distributions of free (aaa), mono- (aae), di- (aee) and triesterified (eee) trimethylolpropanes (T). The three esterification steps of T giving aae, aee and eee give rise

$^{13}$C n.m.r. spectrometry

$^{13}$C n.m.r. spectra were recorded with polyester solutions in DMSO-$d_6$ and/or polyester gels swollen in DMSO-$d_6$ and CDC$_2$–CDC$_2$ (tetrachloroethane, TCE) at 100°C using a Bruker AC 200 spectrometer (50.3 MHz for $^{13}$C). For quantitative determinations using $^1$H inverse gated decoupling sequence, a paramagnetic reagent Cr(acac)$_3$ was added. It has been verified that, for polyester solutions and swollen gels, the conversions did not increase within several days at 100°C. Typical analysis conditions were: pulse angle = 80°, repetition time = 6 s, acquisition time = 3 s for 64 000 words, sweep width = 10 500 Hz, number of scans = 6000–7000.

For overlapped $^{13}$C resonances, quantitative determinations were achieved by simulations using the Bruker LINESIM program.

**Mechanisms of bulk copolyesterification: R. Pétiaud et al.**

**POLYMER, 1992, Volume 33, Number 23 5057**
Mechanisms of bulk copolyesterification: R. Pétiaud et al.

Figure 1. $^{13}$C n.m.r. spectrum of poly(trimethylolpropane azelaate) (1Z+1.15T) obtained in bulk after 0.5h at 180°C. Conversions: COOH(Z)=80%, OH(T)=48%. Underlined letters: origins of the resonances. A, CO acid; E, CO ester; a, CH$_2$O alcohol; e, CH$_3$O ester; aaa, free T; aae, T monoester; aee, T diester; eee, T triester

Figure 1 13C n.m.r. spectrum of poly(trimethylolpropane azelaate) (1Z+1.15T) obtained in bulk after 0.5h at 180°C. Conversions: COOH(Z)=80%, OH(T)=48%. Underlined letters: origins of the resonances. A, CO acid; E, CO ester; a, CH$_2$O alcohol; e, CH$_3$O ester; aaa, free T; aae, T monoester; aee, T diester; eee, T triester

to the splitting of CO esters (Z1+Z9) (172–174 ppm), oxymethylene T1 (61–65 ppm), quaternary carbon T2 (40–44 ppm) and methylene T3 (21–24 ppm) resonances. Even the remote methyl groups T4 (7.4 ppm) resonate with visible shoulders. The distributions of aaa, aae, aee and eee may be easily calculated and cross-checked with relations (2)–(4) (Figure 1).

(i) CH$_2$CH$_3$ (T3, 21–24 ppm). The relative intensities of these resonances are directly proportional to the mole per cent of the three types of esters and free T:

\[
\text{eee \%} = 100 \times \frac{\text{eee}(\text{CH}_2)}{S(\text{CH}_2)} \\
\text{eea \%} = 100 \times \frac{\text{eea}(\text{CH}_2)}{S(\text{CH}_2)} \\
\text{eaa \%} = 100 \times \frac{\text{eaa}(\text{CH}_2)}{S(\text{CH}_2)} \\
\text{aaa \%} = 100 \times \frac{\text{aaa}(\text{CH}_2)}{S(\text{CH}_2)}
\]

\(S(\text{CH}_2)\) is the sum of the four T3 peaks, eee(\text{CH}_2), eea(\text{CH}_2), \ldots, are the relative intensities of the corresponding peaks.

(ii) Quaternary carbon of T (T2, 40–44 ppm). As for T3 resonances, these four well resolved lines are directly proportional to the mole per cent of the four types of T, but unfortunately the eee peak (40.7 ppm) is hidden by DMSO (38–40 ppm). Quantitative determinations can only be achieved if TCE is utilized as n.m.r. solvent.

(iii) CH$_2$O– (T1, 60–65 ppm). The relative intensity of each one of these six lines is proportional to the number \(n\leq3\) of ester (e) and/or alcohol (a) \((n'=3-n)\) groups. One gets (underlined letter(s) = origin(s) of the resonance(s)):

\[
\text{eee \%} = 100 \times \frac{\frac{1}{2}\text{eee}}{S(\text{CH}_2\text{O–e})} \\
\text{eea \%} = 100 \times \frac{\frac{1}{2}\text{eea}}{S(\text{CH}_2\text{O–e})} \\
\text{eaa \%} = 100 \times \frac{\frac{1}{2}\text{eaa}}{S(\text{CH}_2\text{O–a})} \\
\text{aaa \%} = 100 \times \frac{\frac{1}{2}\text{aaa}}{S(\text{CH}_2\text{O–a})}
\]

\(S(\text{CH}_2\text{O–e})\) is the sum of the relative weighted intensities of the three methylene ester peaks in the 63.5–65 ppm region. Similarly:

\[
\text{aaa \%} = 100 \times \frac{\frac{1}{2}\text{aaa}}{S(\text{CH}_2\text{O–a})} \\
\text{ace \%} = 100 \times \frac{\frac{1}{2}\text{ace}}{S(\text{CH}_2\text{O–a})}
\]

\(S(\text{CH}_2\text{O–a})\) is the sum of the relative weighted intensities of the three methylene alcohol peaks in the 60.5–63.5 ppm region.

(iv) CO–e (172–173.5 ppm). These carboxy ester lines, more resolved than their corresponding CH$_2$O–e resonances, are proportional to the number of CO in T(aae,
Mechanisms of bulk copolyesterification: R. Pétiaud et al.

**Conversion of alcohol functions (C(T)).** $C(T)\%$ may be directly determined by using the CH$_2$O–e and CH$_3$O–a sets of resonances:

$$C(T)\% = \frac{100 \times S(e)}{S(e) + S(a)}$$  \hspace{1cm} (6)

with $\Sigma(e)$ (63.5–65 ppm) = eee + eae + aae and $\Sigma(a)$ (60.5–63.5 ppm) = ace + aee + aae.

$C(T)$ and $C(Z)$ (equation (1)) thus calculated may also be cross-checked using the actual COOH/OH ratio ($r$) that may be determined by comparing $Z_3$ (24.7 ppm) and $T_3$ (21–23.5 ppm). In the present case $r=0.59$ instead of 0.58:

$$C(T) = rC(Z)$$  \hspace{1cm} (7)

The results are in good agreement within experimental errors.

**Figure 2** shows the typical variations of $C(T)$, $C(Z)$ and the distributions of the four T species (aaa, aae, aee and eee) against reaction times of the mixture (1Z + 1.15T) at 180°C. It is worth noting that, in the first 0.5 h, the polyesterification reaction is very fast. But, between 2 and 4 h, the conversions seem to reach asymptotic limits ($C(T)=57\%$ and $C(Z)=96\%$—Figure 2a), and correspondingly, no large variations are observed in the distributions of the four T species (Figure 2b). Particularly, the proportion of triesterified T(eee) only slightly increases from 18% to 19%, that is, within experimental errors.

In bulk, the obtained poly-TZ (TZ(I), Table 2) appears like a gel, but in DMSO the solution of TZ(I) is quite homogeneous and relatively mobile with only traces of microgels. Thus the gel state observed in bulk should be more likely a physical gel due mostly to Van der Waals links between linear chains.

Even with $r=0.667$, the (1Z + 1T) mixture gives a physical gel after 3.5 h (TZ(II)) at 180°C (mobile solution in DMSO). Only after 12 h at the same temperature, the obtained sample TZ(III) gives a dense chemically reticulated gel. **Figure 3** compares the carboxy and oxymethylene resonances of these two samples. The spectrum of the solution of TZ(II) does not differ markedly from the one of TZ(I), with resonance lines of 3.5 Hz and 5 Hz in width at half-height for CH$_2$O eea (64 ppm) and CH$_3$O eee (63.6 ppm) respectively. The same resonances of the dense ZT(III) gel are severely broadened (5 Hz and 9 Hz for the same two lines respectively) and shifted towards high fields. Quantitative determinations are reported in Table 2.

**Bulk polyesterification of (1P + 0.8T) at 180°C**

A typical $^{13}$C n.m.r. spectrum of poly(trimethylolpropane o-phthalate) (poly-TP, see Scheme 1) is shown in **Figure 4**. Because of the aromatic effects of P, compared to the poly-TZ spectrum (**Figure 3**), the methylene esters of P resonate at lower fields (64.6–66.2 ppm), while the
Mechanisms of bulk copolyesterification: R. Pétiaud et al.

hydroxylated ones resonate at higher fields (60.5–62.5 ppm). Besides, because of the mutual effects of the two near carbonyl groups, the CO resonances allow discrimination between diesterified (P(EE), 166.2–166.9 ppm), monoesterified (P(EA), 166.9–167.3; and P(EA), 167.7–168.3 ppm) and free o-phthalic acid (P'(AA), 168.5 ppm) (Figure 5). P'(AA) should result from the hydrolysis of P by traces of water from DMSO. The presence of free o-phthalic anhydride may only be shown in TCE. Again, each one of the three resonances of CO (AE, AE, EE) is split into three peaks by T(aae, aee and eee). The same broadening phenomenon—due to steric hindrance—is observed for CO and CH₂O resonances.

Conversions of acid functions of o-phthalic anhydride (C(P)) and distributions of EE%, EA% and AA% of P units using CO resonances. Here the CO acids of P belong to AA (168.5 ppm) and AE (167.7–168.3 ppm), and those of CO esters to AE (166.8–167.3 ppm) and EE (166.2–166.9 ppm). (AE) equals (AE) in relative intensities. Thus one gets (Figure 6a):

\[
C(P) \% = 100 \times \frac{(AE)+(EE)}{(AA)+(AE)+(AE)+(EE)}
\]

(8)

(AA), (AE),... are relative intensities of underlined groups. For the distributions, one has (Figure 6b):

\[
AA \% = 100 \times \frac{(AA)}{(AA)+(AE)+(AE)+(EE)}
\]

(9)

\[
AE \% = 100 \times \frac{(AE)}{(AA)+(AE)+(AE)+(EE)}
\]

\[
EE \% = 100 \times \frac{(EE)}{(AA)+(AE)+(AE)+(EE)}
\]

Conversions of alcohol functions of T(C(T) %) and distributions of T(aaa, aae, ace and eee). Equation (6) may be used here with \( \Sigma_a \) (64.6–66.2 ppm) and \( \Sigma_e \) (60.5–62.6 ppm)

Figure 3 13C n.m.r. spectra of poly(trimethylolpropane azelate) (1Z + 1T) obtained in bulk at 180°C after 3.5 h (b, solution) and 12 h (a, swollen gel). Enlargement of CO and CH₂O (T1) resonances. See notes of Figure 1 and text

Figure 4 13C n.m.r. spectrum of poly(trimethylolpropane o-phthalate) (1P+0.8T) obtained in bulk after 2 h at 180°C. Conversions: COOH(P)=82%, OH(T)=71%. AA, diacid P; AE, monoesterified P; for a, e, etc., see notes of Figure 1 and text

5060 POLYMER, 1992, Volume 33, Number 23
Mechanisms of bulk copolyesterification. R. Pétiaud et al.

for the determination of $C(T)\%$. Similarly, relations (2)-(5) give the distributions of T(aaa, aae, aee and eee).

The results are reported in Figures 6a and 6c. As was observed for the (1Z+1.15T) mixture, the polyesterification is very fast during the first 0.5 h (Figure 6a), then the esterification rate decreases. In contrast with Z, here the evolutions of the distributions of the four T species (aaa–eee, Figure 6c) seem to go on beyond 4 h, mainly in favour of T(eee). Again, about 2 mol\% of free (probably trapped) T are found even after 4 h of reaction.

Critical conversions of acid functions ($C_\alpha$); physical and covalent (reticulated) gels of the binary systems

In spite of the apparent gel states observed in bulk, samples TZ(I) (1Z+1.15T), TZ(II) (1Z+1T) and TP (1P+0.8T) are soluble in DMSO, in contrast with TZ(III) (1Z+1T), which actually gives an insoluble swollen gel (Tables 2 and 3).

If the simplest statistical approach of Flory and Stockmeyer (FS) is considered, assuming that the same type of function (alcohol or acid) has the same reactivity whatever the conversions may be, the critical conversions of acid ($C_\alpha(FS)$) from which the polyester becomes gelled is given by:

$$C_\alpha(FS) = \left\{ r \left[ 1 + \rho (f_T - 2) \right] \right\}^{-1/2}$$

$$C_\alpha(FS) = (2r)^{-1/2}$$

The different values of $C_\alpha(FS)$ (equations (10) or (11)) and the observed conversions of acid $C(Z)$ (equation (1)) and $C(P)$ (equation (8)) are reported in Tables 2 and 3.

Figure 6 Polyesterification of o-phthalic anhydride (P, 1 mol) and trimethylolpropane (T, 0.8 mol) (COOH/OH=0.83) in bulk at 180°C. Variations versus time. (a) Conversions of alcohol and acid. (b) Distributions of diesterified (EE), monoesterified (EA) and o-phthalic acid (AA). (c) Distributions of triesterified (eee), diesterified (eea), monoesterified (eaa) and free T (aaa).
Mechanisms of bulk copolyesterification: R. Pétiaux et al.

$C_c(FS)$ values may only be considered as threshold critical conversions; because of the steric hindrances of the reagents and the increasing viscosity of the reaction mixtures, (i) the reactivities of OH and COOH decrease as the conversions increase (Figures 2 and 3), (ii) T cannot be entirely triesterified and (iii) trapped free T (3–5 mol%) is found (even after 24 h at 180°C for TZ(III)—Table 3), so the actual critical conversions ($C_{c,obs}$) must be larger than the theoretical ones $C_c(FS)$.

For (1Z + 1T) (Table 2), $C_{c,obs}(Z)$ should be between 94% (TZ(II)) and 99% (TZ(III)), and is much larger than $C_c(Z)(FS)=87\%$. Moreover, there is no great difference in the distribution of T esters between the physical gel TZ(II) and the dense covalent gel TZ(III). The potential triester crosslinking units (T eee) only slightly increase from 21% to 23%, so it is plausible to assume that crosslinking reactions should partly proceed via transesterification between branches.

With $r=0.83$, the (1P + 0.8T) mixture (Table 3) should theoretically be more capable of reticulation. But even at $C(P)=82\% > C_c(P)(FS)=77\%$, no gel was observed. Besides the preceding causes, the tendency to give cycles by intramolecular reactions between the side branches.

COPOLYESTERIFICATION IN BULK OF

(0.5Z + 0.5P + 0.8T)

Conversions and distributions of different copolyester species

Typical spectra are shown in Figures 7 and 8. The variations of the conversions of acid ($C(Z)$), (C(P)) and alcohol (C(T)) functions, and the distributions of P(AA, AE, EE) and T(aaa, aae, aee, eee) versus time are illustrated in Figure 9. Table 3 compares the chemical characteristics of the three systems (1P + 0.8T), (1Z + 0.8T) and (0.5Z + 0.5P + 0.8T) having the same $r$, at the same conversions. It is instructive to note that the increasing ability to give covalent gels is: (1P + 0.8T) < (0.5Z + 0.5P + 0.8T) < (1Z + 0.8T). The richer the mixture in Z component, the easier it gels. At 82% of conversion in acid, (1Z + 0.8T) is a dense gel (Table 3), whereas (1P + 0.8T) gives a mobile solution with only traces of tiny gels. For the last one, part of the T(eea) diesters and T(eee) triesters should be cyclized by P(EE) diesters.

For all systems containing P, microgels should actually be produced from the very beginning of the reaction because nearly the whole o-phthalic acid (P'(AA)~5%) found in DMSO-d$_6$ (Figure 7) results from the hydration of trapped o-phthalic anhydride (P(AA)~4 mol%) (Figures 8 and 9, Table 3): carbons $P_2$ and $P_3$ resonate at 125.5 and 135.9 ppm respectively in anhydrous TCE.

The same phenomenon is observed with T(aaa=3–5 mol%, Table 3).

Because of the chain length, Z should not cyclize on the same T unit and thus poly-TZ gels more readily: at 180°C, the (1Z + 0.8T) system already gives a dense covalent gel after 1.58 h with $C(Z)=82\%$ (Table 3), whereas (1P + 0.8T) does not reticulate at the same acid.

Figure 7 13C n.m.r. spectrum of a gelled copolyester of azelaic acid (Z, 0.5 mol) +o-phthalic anhydride (P, 0.5 mol)+trimethylolpropane (T, 0.8 mol) after 3.5 h at 180°C. Solvent, DMSO-d$_6$; temperature, 100°C. Conversions: COOH(Z)=96%; COOH(P)=63%; OH(T)=69%. A, E, a and c: see notes of Figures 1 and 2 and text.
Mechanisms of bulk copolyesterification: R. Pétauad et al.

Conversion $C(P)$ (Table 3). In ternary $(Z+P+T)$ systems, the increasing ease of reticulation should parallel the increasing concentration in $Z$ component.

As n.m.r. solvents, DMSO and TCE give complementary information. If better resolved resonances of CO (166–174 ppm), $T_2$(aae and aee) (41.5–43 ppm) and $T_3$(21–24 ppm) are obtained with DMSO, $T_2$(eee) peaks are hidden (~41 ppm, Figure 10a). In contrast, in TCE, trapped free $P$s have been shown and the $T_2$(eee) composite resonances may be quantitatively studied (Figure 10b).

Table 3 Polyestersifications of o-phthalic anhydride ($P$, 1 mol)+ trimethylolpropane ($T$, 0.8 mol), azelaic acid ($Z$, 1 mol)+$T$ (0.8 mol) and copolyesterification of $P$ (0.5 mol)+$Z$ (0.5 mol)+$T$ (0.8 mol) in bulk at 180°C—quantitative determinations by $^{13}$C n.m.r.: solvent, DMSO-d$_6$; 90–100°C; relaxation reagent, Cr(Acac)$_2$; A and E, acid and ester groups of $P$; a and e, alcohol and ester groups of $T$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Gel state</th>
<th>Conversion (%)</th>
<th>Distributions (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP</td>
<td>No</td>
<td>71</td>
<td>P(AA) 2 P(AE) 33</td>
</tr>
<tr>
<td>TZP</td>
<td>Covalent</td>
<td>71</td>
<td>P(AE) 33 P(EE) 65</td>
</tr>
<tr>
<td>TZ(IV)</td>
<td>Covalent</td>
<td>83</td>
<td>T(aaa) 3 T(aae) 20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>83</td>
<td>T(aee) 44 T(eee) 32</td>
</tr>
</tbody>
</table>

* Equations (2), (6), (7)
* Equation (1)
* Equation (8)
* Equations (10), (11)
* Obtained using 0.5($C(Z)$+$C(P)$)
* Equation (9)
* Equations (2)–(5)
Mechanisms of bulk copolyesterification: R. Pétaud et al.

Figure 9 Copolyesterification of azelaic acid (Z, 0.5 mol), α-phthalic anhydride (P, 0.5 mol) and trimethylolpropane (T, 0.8 mol) in bulk at 180°C. Variations versus time. (a) Conversions of acid (Z, P) and alcohol (T). (b) Distributions of diesterified (EE), monoesterified (EA) and free P (AA). (c) Distributions of triesterified (eee), diesterified (eea), monoesterified (eaa) and free T (aaa).

and (TPPP, (TPPP + TPZP + TZPP), (TPZZ + TZPZ + TZZP), TZZZ) respectively. In diesters and triesters, the order of P and Z is the one of the corresponding esterification steps (for example, TPZP: first, second and third esterifications of T by P, Z and P respectively).

Statistics of mono- and diesterifications of T. Quantitative determinations by using CO resonances (Figures 7 and 8) give C(Z) = 97% and C(P) = 69%, so the probabilities of presence of Z (p(Z)) and P (p(P)) in the whole copolyester are:

\[ p(P) = \frac{69}{97 + 69} = 0.42 \]
\[ p(Z) = \frac{97}{97 + 69} = 0.58 \]

with

\[ p(P) + p(Z) = 1 \]

In the 42.5-43.0 ppm region of Figure 10a, the normalized relative intensities of the two peaks belonging to \( T_2(aae) \) are 0.43 and 0.57 for the lines at 42.93 and 42.76 ppm respectively. Thus it is plausible to assign the \( T_2 \) of TP to the line at lower field. One has:

\[ p(P) = 0.43 \text{ for TP (42.93 ppm)} \]
\[ p(Z) = 0.57 \text{ for TZ (42.76 ppm)} \]

The fact that the proportions of TP and TZ equal the global proportions of P and Z in the whole copolyester suggests that the monoesterifications of T by P and Z are proportional to their relative reactivities, Z being 1.3 \((0.57/0.43)\) times more reactive than P.

If it is assumed that these relative reactivities remain the same for diesterifications—in other words if the second steps of esterification (giving TPP, TPZ or TZP and TZZ) should not depend on the nature of the monoesters (TP or TZ)—the copolyesterification should be Bernoullian (no penultimate effects) and one should have:

\[ p(P) = p(P/P) = p(P/Z) = 0.43 \]
\[ p(Z) = p(Z/P) = p(Z/Z) = 0.57 \]

Figure 10 13C n.m.r. spectra of a gelled copolyester of azelaic acid (Z, 0.5 mol) + α-phthalic anhydride (P, 0.5 mol) + trimethylolpropane (T, 0.8 mol) after 3.5 h at 180°C. Swollen gel in DMSO-d6 (a) and CDCl3 (b). Temperature, 100°C. Enlargement of the resonances of T quaternary carbons (40-44 ppm). TZ, TP, mono azelaate and α-phthalate of T; TZP, mixed diester (azelaate, α-phthalate) of T, etc.
Mechanisms of bulk copolyesterification. R. Pétaud et al.

Here $p(P/Z)$ is the conditional probability of esterification of the second T's hydroxyl by P, the first one being esterified by Z giving TZ, etc. There are two ways to obtain the two mixed diesters depending on the nature of the monoesters (TP or TZ) resulting from the first esterifications:

$$TP + Z = TPZ \quad \text{and} \quad TZ + P = TZP$$

$$TP + TZP = TPZ^+$$

This simplifying hypothesis allows the calculations of the probabilities of the presence of these three types of diesters as follows:

$$p(PP) = p(P)p(P/Z) = p(P)^2$$

$$p(PZ)^+ = p(PZ) + p(ZP)$$

$$= p(P)p(Z/P) + p(Z)p(P/Z) = 2p(P)p(Z)$$

$$p(ZZ) = p(Z)p(Z/Z) = p(Z)^2$$

$$p(PP) + p(PZ)^+ + p(ZZ) = 1$$

The identification of the three lines in the 41.7-42.3 ppm region (Figure 10a) is made by comparing their normalized relative intensities to the calculated probabilities of presence (Table 4). Thus, diesterifications as well as monoesterifications follow Bernoullian statistics, and it is informative to note that the proportion of mixed diesters TPZ$^+$ is the largest.

Statistics of triesterifications of T. There are four types of triesters T(eee), and two of them are mixed: TPPP, TPPZ, TPZZ and TZZZ. Mixed triesters may be formed in three different ways, owing to the order of esterifications by P and/or Z. If Bernoullian statistics are assumed, again one gets:

$$p(PPP) = p(P)^3$$

$$p(PPZ)^+ = 3[p(P)^2p(Z)]$$

$$p(PZZ)^+ = 3[p(P)p(Z)^2]$$

$$p(ZZZ) = p(Z)^3$$

Thus:

$$p(PPP) = p(P)^3$$

$$p(PPZ)^+ = 3[p(P)^2p(Z)]$$

$$p(PZZ)^+ = 3[p(P)p(Z)^2]$$

$$p(ZZZ) = p(Z)^3$$

Table 4

<table>
<thead>
<tr>
<th>Calculated probabilities of presence</th>
<th>Observed normalized intensities (simulation)</th>
<th>$T_2(\delta, ppm)$ (in DMSO)</th>
<th>Diesters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p(PP)=0.185$</td>
<td>0.20 42.05</td>
<td>TPP</td>
<td></td>
</tr>
<tr>
<td>$p(PZ)^+=0.49$</td>
<td>0.49 41.89</td>
<td>TPS</td>
<td></td>
</tr>
<tr>
<td>$p(ZZ)=0.325$</td>
<td>0.31 41.74</td>
<td>TZZ</td>
<td></td>
</tr>
</tbody>
</table>

The four calculated probabilities of presence allow the identification of the four Lorentzian peaks obtained by simulation of the $T_2(\text{eee})$ carbon resonances in the 40.8-41.7 ppm region recorded in TCE (Figure 10b). The most probable assignment is as shown in Table 5.

Within experimental errors, the good agreement between calculated probabilities of presence and normalized relative intensities of simulated peaks leads in favour of Bernoullian distributions of the triesters (as for mono- and diesters) in the covalent gel obtained after 3.5 h at 180°C. It is instructive to note that 70% of the T(eee)s (or 70% x 0.34=24% of T) are mixed triesters (TPPZ$^+ + TPZZ^+$).

Because of the chain length of Z, poly-TZ gels more easily than poly-TP. At 180°C, the (1Z+0.8T) system gives a dense covalent gel with $C(Z)=82\% (> C_{(FS)}=77\%)$ at 1.58 h (Table 3), whereas only mobile solution is observed with $C(Z)=79\%$. The actual critical conversion of COOH(Z) ($C(Z)$) should be found between 79% and 82%. In contrast, even with $C(P)=82\%$ after 4 h at 180°C, (1P+0.8T) gives no gel (Figure 6, Table 3). It is thus plausible to assume that the more T(eee) units have Z branches, the easier is the formation of covalent Z links between copolyester chains. The increasing ease of reticulation should be:

$$\text{TPPP} < \text{TPPZ} < \text{TPZZ} < \text{TZZZ}$$

Finally, with $r=0.83$ and in the presence of Z, covalent gels should only be observed around 82-83% of conversion of acid if T(eee)$\approx 34-35\%$.

REFERENCES

1 Deschêres, I. and Pham, Q. T. Makromol. Chem. 1990, 191, 891
6 Wals, G. J. Oil Col. Chem. Assoc. 1977, 60, 11
7 Geoghegan, J. T. and Bambrick, W. F. J. Paint Technol. 1970, 42 (548), 490

POLYMER, 1992, Volume 33, Number 23 5065