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

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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: copolyesters; nuclear magnetic resonance spectroscopy; polyesterification; azelaic acid; *o*-phthalic anhydride; trimethylolpropane; gelation)

INTRODUCTION

Copolyesters 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 syntheses, 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 copolyesters 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[1].

Though many polyols[2,3] (with three or more alcohol functions per molecule)—like glycerol, trimethylolethane, 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 acid (P′) were found in P. The ^{13}C chemical shifts of T, Z, P and P′ are reported in *Table 1*.

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† Systematic names: azelaic acid = nonanedioic acid; trimethylolpropane = 2,2-bis(hydroxymethyl)butan-1-ol

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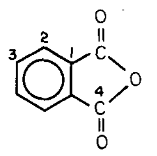
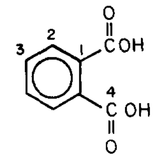
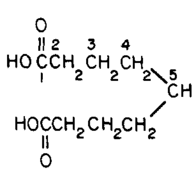
Table 1 ^{13}C n.m.r. chemical shifts of trimethylolpropane (T), *o*-phthalic anhydride (P), *o*-phthalic acid (P′) and azelaic acid (Z): solvent, DMSO-d_6; room temperature

	δ (ppm)				
Structure	1	2	3	4	5
T $(\overset{1}{HOCH_2})_3\overset{2}{C}\,\overset{3}{CH_2}\overset{4}{CH_3}$	61.76	43.28	21.20	7.40	
P 	131.18	125.41	136.28	163.11	
P′ 	132.97	128.39	130.66	168.60	
Z 	174.65	33.89	24.70	28.70	28.70

Polyesterifications

Five mixtures with different COOH/OH ratios (r) have been studied (quantities of reagents are expressed in moles):(1Z+1.15T) ($r=0.58$), (1Z+1T) ($r=0.67$) and (1P+0.8T), (1Z+0.8T), (0.5Z+0.5P+0.8T) ($r=0.83$). Reactions were performed in bulk at 180°C in a cylindrical 2 litre vessel with strong mechanical stirring. As the reactions proceeded, the viscosity of the mixtures increased, and for three mixtures, the mechanical stirring became inoperative: after 3.5 h for (1Z+1T) (sample TZ(II)) and (0.5Z+0.5P+0.8T) (sample TZP) and after 1.58 h for (1Z+0.8T) (sample TZ(IV)). The three samples TZ(II), TZP and TZ(IV) thus obtained were considered as gelled. But in dimethylsulphoxide (DMSO), TZ(II) gave a viscous solution, whereas TZP and TZ(IV) were swollen gels. Insoluble dense gel TZ(III) was derived from TZ(II) after an additional 12 h curing at 180°C. Reactions were stopped by rapid cooling.

^{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 $CDCl_2$–$CDCl_2$ (tetrachloroethane, TCE) at 100°C using a Bruker AC 200 spectrometer (50.3 MHz for ^{13}C). For quantitative determinations using ^1H 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.

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 are mono-, di- and triesterified T respectively) by the acid functions of azelaic acid (Z) or/and *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 polyesterifications 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

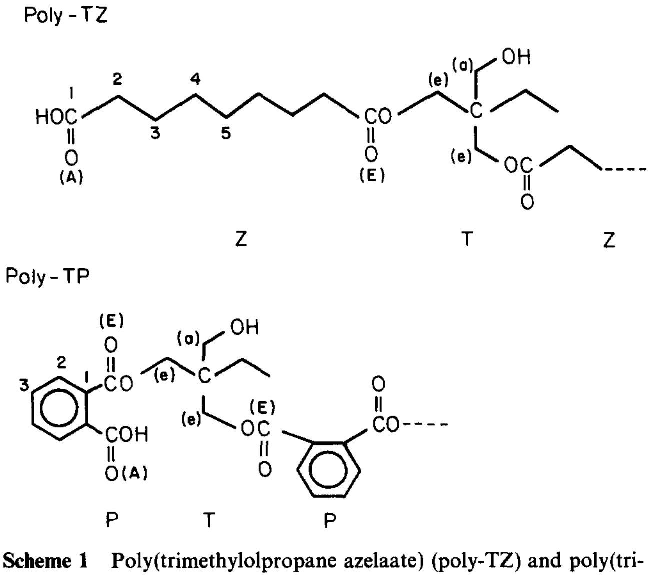
Bulk polyesterifications of (1Z+1.15T) and (1Z+1T)

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.

Conversion of acid functions of azelaic acid (C(Z)). With azelaic acid, because of the long methylene chain, the COOHs of diacid ($\underline{AA}$) and monoacid monoester ($\underline{A}E$) 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 ($\underline{CO}OCH_2$, three peaks in the 171.5–173.5 ppm region) (see *Figure 3*):

$$C(Z)\ \% = 100 \times \frac{(\underline{CO}OCH_2)}{(COOH)+(\underline{CO}OCH_2)} \qquad (1)$$

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



Scheme 1 Poly(trimethylolpropane azelaate) (poly-TZ) and poly(trimethylolpropane *o*-phthalate) (poly-TP). Z, azelaic acid; P, *o*-phthalic anhydride; T, trimethylolpropane; A, COOH; E, CO ester; a, alcohol group; e, methylene ester

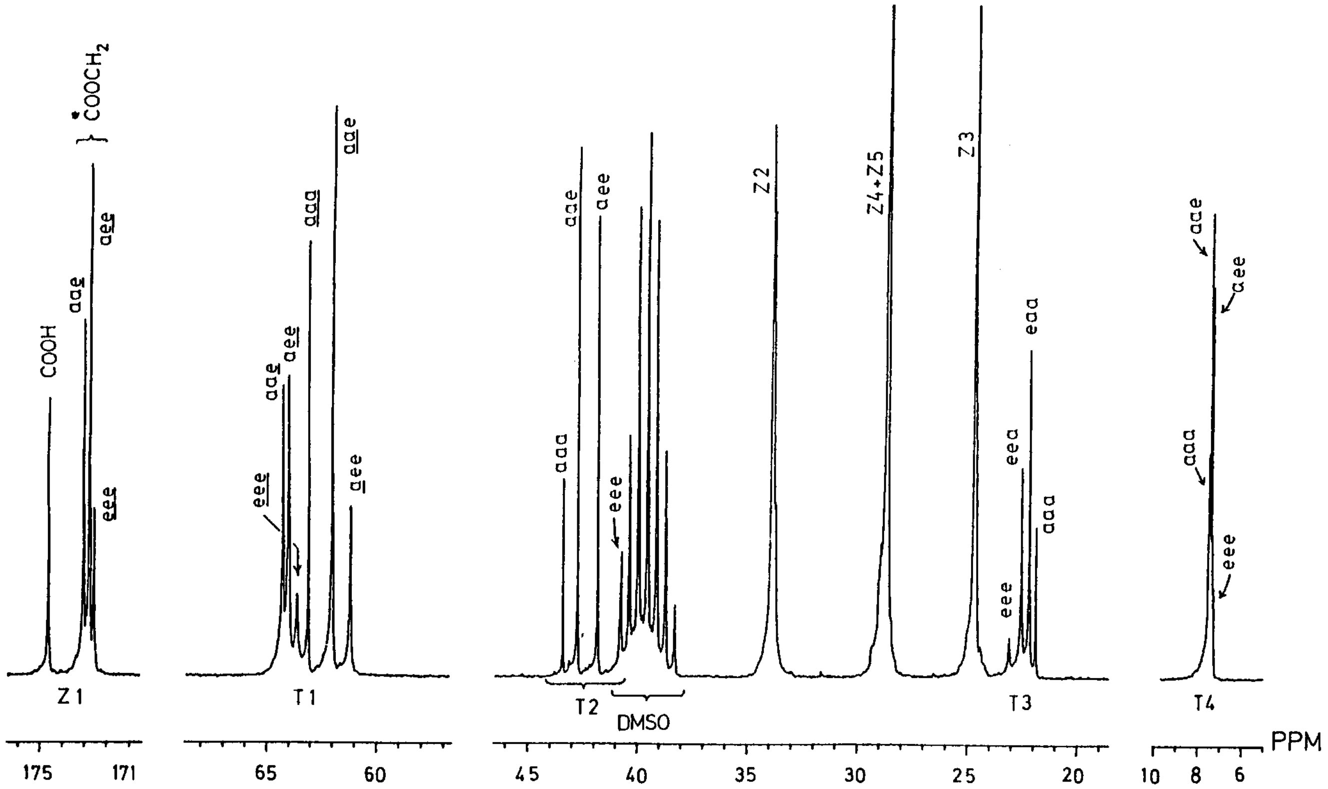


Figure 1 ^{13}C n.m.r. spectrum of poly(trimethylolpropane azelaate) (1Z+1.15T) obtained in bulk after 0.5 h at 180°C. Conversions: COOH(Z)=80%, OH(T)=48%. Underlined letters: origins of the resonances. A, CO acid; E, CO ester; a, CH_2O alcohol; e, CH_2O ester; aaa, free T; aae, T monoester; aee, T diester; 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) $\underline{CH_2}CH_3$ (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:

$$\begin{aligned}\mathrm{eee}\ \% &= 100\times\frac{\mathrm{eee}(\mathrm{CH_2})}{S(\mathrm{CH_2})}\\ \mathrm{eea}\ \% &= 100\times\frac{\mathrm{eea}(\mathrm{CH_2})}{S(\mathrm{CH_2})}\\ \mathrm{eaa}\ \% &= 100\times\frac{\mathrm{eaa}(\mathrm{CH_2})}{S(\mathrm{CH_2})}\\ \mathrm{aaa}\ \% &= 100\times\frac{\mathrm{aaa}(\mathrm{CH_2})}{S(\mathrm{CH_2})}\end{aligned}\tag{2}$$

$S(CH_2)$ is the sum of the four T3 peaks, eee(CH_2), eea(CH_2),..., 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_2O– (T1, 60–65 ppm). The relative intensity of each one of these six lines is proportional to the number ($n \leqslant 3$) of ester (e) and/or alcohol (a) ($n' = 3\text{-}n$) groups. One gets (underlined letter(s) = origin(s) of the resonance(s)):

$$\begin{aligned}\mathrm{eee}\ \% &= 100\times\frac{\frac{1}{3}\underline{\mathrm{eee}}}{S(\mathrm{CH_2O{-}e})}\\ \mathrm{eea}\ \% &= 100\times\frac{\frac{1}{2}\underline{\mathrm{ee}}\mathrm{a}}{S(\mathrm{CH_2O{-}e})}\\ \mathrm{eaa}\ \% &= 100\times\frac{\underline{\mathrm{e}}\mathrm{aa}}{S(\mathrm{CH_2O{-}e})}\\ S(\mathrm{CH_2O{-}e}) &= \tfrac{1}{3}\underline{\mathrm{eee}}+\tfrac{1}{2}\underline{\mathrm{ee}}\mathrm{a}+\underline{\mathrm{e}}\mathrm{aa}\end{aligned}\tag{3}$$

$S(CH_2O–e)$ is the sum of the relative weighted intensities of the three methylene ester peaks in the 63.5–65 ppm region. Similarly:

$$\begin{aligned}\mathrm{aaa}\ \% &= 100\times\frac{\frac{1}{3}\underline{\mathrm{aaa}}}{S(\mathrm{CH_2O{-}a})}\\ \mathrm{aae}\ \% &= 100\times\frac{\frac{1}{2}\underline{\mathrm{aa}}\mathrm{e}}{S(\mathrm{CH_2O{-}a})}\\ \mathrm{aee}\ \% &= 100\times\frac{\underline{\mathrm{a}}\mathrm{ee}}{S(\mathrm{CH_2O{-}a})}\\ S(\mathrm{CH_2O{-}a}) &= \tfrac{1}{3}\underline{\mathrm{aaa}}+\tfrac{1}{2}\underline{\mathrm{aa}}\mathrm{e}+\underline{\mathrm{a}}\mathrm{ee}\end{aligned}\tag{4}$$

$S(CH_2O–a)$ 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_2O–e resonances, are proportional to the number of CO in T(aae, aee and eee). Similarly to equations (3), one gets:

$$\text{aae } \% = 100 \times \frac{\text{aae(CO–e)}}{S\text{(CO–e)}}$$

$$\text{aee } \% = 100 \times \frac{\frac{1}{2}\text{aee(CO–e)}}{S\text{(CO–e)}} \qquad (5)$$

$$\text{eee } \% = 100 \times \frac{\frac{1}{3}\text{eee(CO–e)}}{S\text{(CO–e)}}$$

S(CO–e) is the sum of the relative weighted intensities of these three CO–e lines.

Conversion of alcohol functions (C(*T*)). C(T) % may be directly determined by using the CH_2O–e and CH_2O–a sets of resonances:

$$C\text{(T) } \% = \frac{100 \times S_e}{\Sigma_e + \Sigma_a} \qquad (6)$$

with Σ_e(63.5–65 ppm) = eee + eea + eaa and Σ_a(60.5–63.5 ppm) = aee + aae + aaa.

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 Z3 (24.7 ppm) and T3 (21–23.5 ppm). In the present case $r = 0.59$ instead of 0.58:

$$C\text{(T)} = rC\text{(Z)} \qquad (7)$$

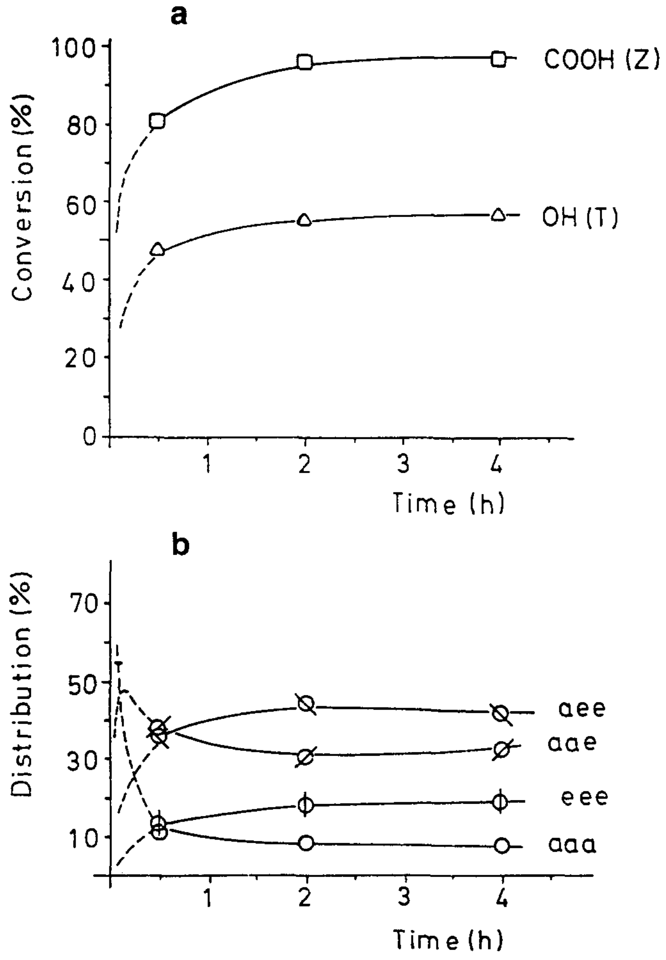


Figure 2 Polyesterification of azelaic acid (Z, 1 mol) and trimethylolpropane (T, 1.15 mol) (COOH/OH = 0.58) in bulk at 180°C. Variations *versus* time. (a) Conversions of alcohol and acid. (b) Distributions of free (aaa), mono- (aae), di- (aee) and triesterified T (eee)

Table 2 Polyesterifications in bulk at 180°C of azelaic acid (Z, 1 mol) + trimethylolpropane (T, 1.15 mol) and Z (1 mol) + T (1 mol)—quantitative determinations by ^{13}C n.m.r.: solvent, DMSO-d_6; 100°C; relaxation reagent, Cr(Acac)$_3$; a, alcohol; e, ester

	1Z + 1.15T	1Z + 1T	
r = COOH/OH	0.58	0.67	
Reaction time (h)	4	3.5	12
Sample	TZ(I)	TZ(II)	TZ(III)
Gel state	No	Physical	Covalent
Conversions (%)			
alcohol (C(T))[a]	57[d]	61[d]	63[d]
acid (C(Z))[b]	96	94	99
acid (C_C(FS))[c]	93	87	
Distribution (%) of T[e]			
aaa	7	5	4
aae	33	29	29
aee	42	45	44
eee	19	21	23

[a] Equation (5)
[b] Equation (1)
[c] Equations (10), (11)
[d] Equation (7) gives values 54, 63 and 66 respectively
[e] Equation (4)

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_2O $\underline{\text{eea}}$ (64 ppm) and CH_2O $\underline{\text{eee}}$ (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 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($\underline{E}$A), 166.9–167.3; and P(E$\underline{A}$), 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 ($\underline{A}$E, A$\underline{E}$, $\underline{EE}$) is split into three peaks by T(aae, aee and eee). The same broadening phenomenon—due to steric hindrance—is observed for CO and CH_2O resonances.

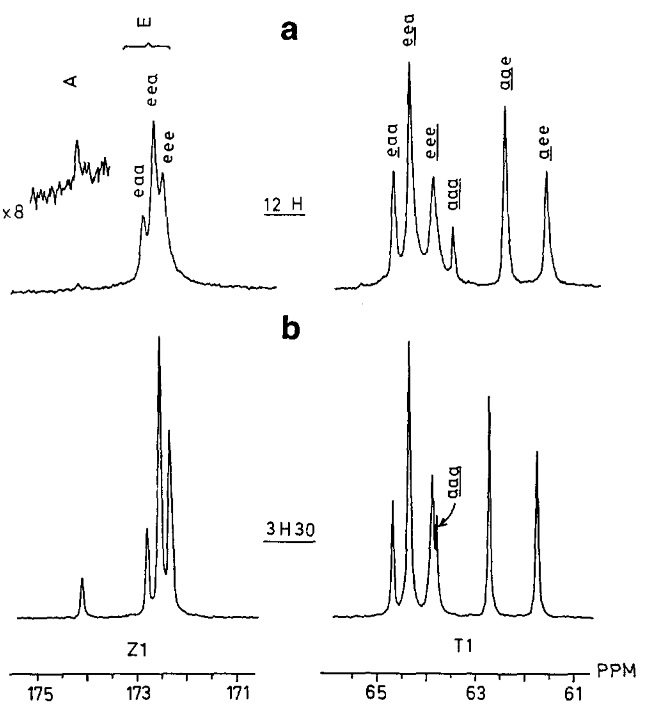


Figure 3 ^{13}C n.m.r. spectra of poly(trimethylolpropane azelaate) (1Z + 1T) obtained in bulk at 180°C after 3.5 h ((b), solution) and 12 h ((a), swollen gel). Enlargement of CO and CH_2O (T1) resonances. See notes of *Figure 1* and text

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 $\underline{AA}$ (168.5 ppm) and $\underline{A}$E (167.7–168.3 ppm), and those of CO esters to A$\underline{E}$ (166.83–167.3 ppm) and $\underline{EE}$ (166.2–166.9 ppm). ($\underline{A}$E) equals (A$\underline{E}$) in relative intensities. Thus one gets (*Figure 6a*):

$$C(\mathrm{P})\ \% = 100 \times \frac{(\mathrm{A\underline{E}}) + (\underline{\mathrm{EE}})}{(\underline{\mathrm{AA}}) + (\underline{\mathrm{A}}\mathrm{E}) + (\mathrm{A\underline{E}}) + (\underline{\mathrm{EE}})} \qquad (8)$$

($\underline{AA}$), ($\underline{A}$E),... are relative intensities of underlined groups. For the distributions, one has (*Figure 6b*):

$$\mathrm{AA}\ \% = 100 \times \frac{(\underline{\mathrm{AA}})}{(\underline{\mathrm{AA}}) + (\underline{\mathrm{A}}\mathrm{E}) + (\mathrm{A\underline{E}}) + (\underline{\mathrm{EE}})}$$

$$\mathrm{AE}\ \% = 100 \times \frac{(\underline{\mathrm{A}}\mathrm{E})\ \text{or}\ (\mathrm{A\underline{E}})}{(\underline{\mathrm{AA}}) + (\underline{\mathrm{A}}\mathrm{E}) + (\mathrm{A\underline{E}}) + (\underline{\mathrm{EE}})} \qquad (9)$$

$$\mathrm{EE}\ \% = 100 \times \frac{(\underline{\mathrm{EE}})}{(\underline{\mathrm{AA}}) + (\underline{\mathrm{A}}\mathrm{E}) + (\mathrm{A\underline{E}}) + (\underline{\mathrm{EE}})}$$

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

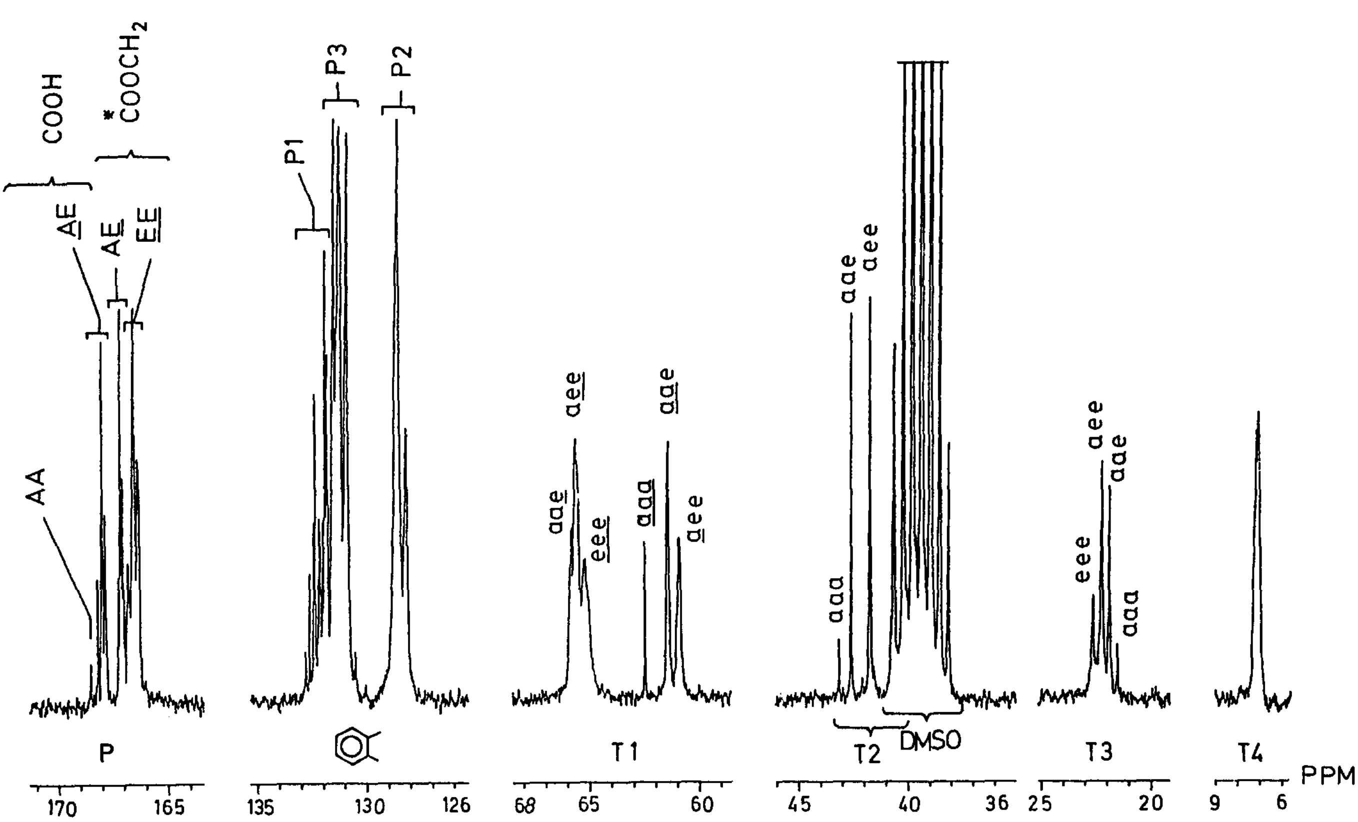


Figure 4 ^{13}C n.m.r. spectrum of poly(trimethylolpropane *o*-phthalate) (1P + 0.8T) obtained in bulk after 2 h at 180°C. Conversions: COOH(P) = 82%, OH(T) = 71%. AA, diacid P; AE, monoesterified P; for a, e, etc., see notes of *Figure 1* and text

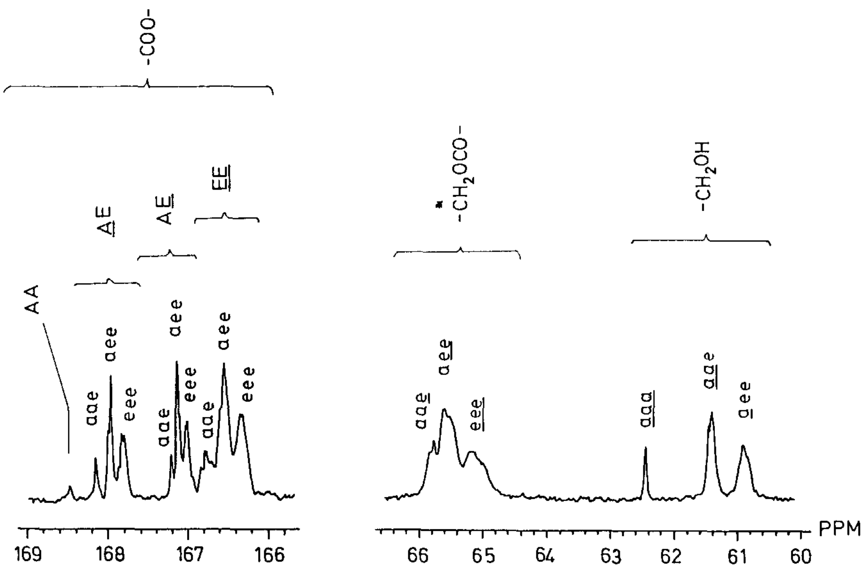
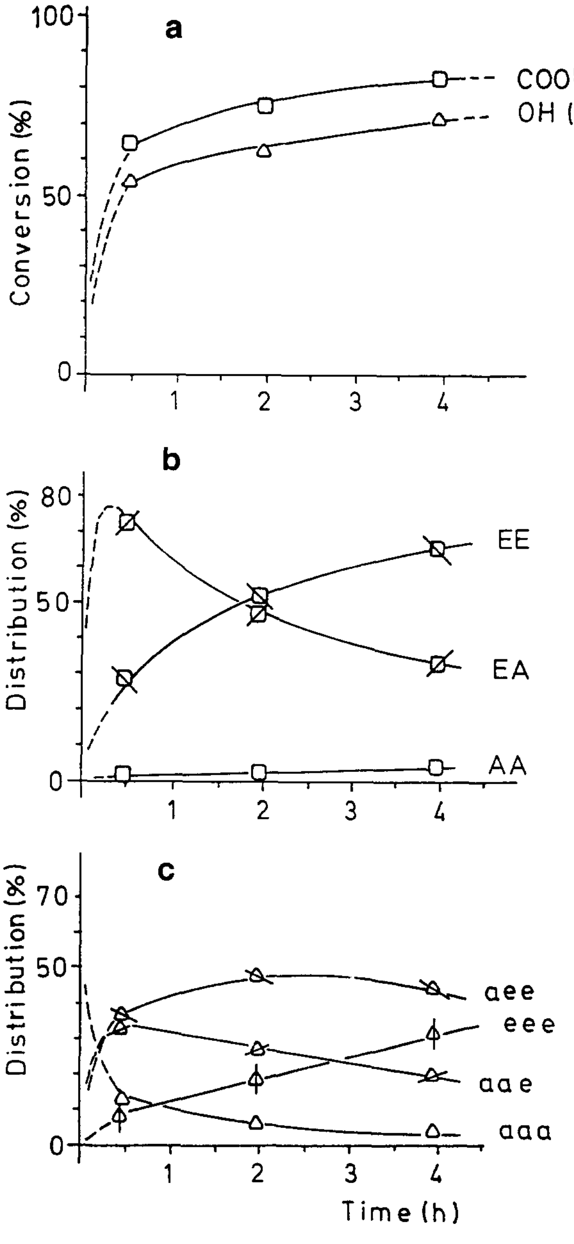


Figure 5 ^{13}C n.m.r. spectra of poly(trimethylolpropane *o*-phthalate) (1P+0.8T) obtained in bulk after 2h at 180°C. Enlargement of CO and CH_2O (T_1) resonances. See notes of *Figure 4* and text



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_c)*; 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_c(FS)) from which the polyester becomes gelled is given by[4]:

$$C_c(\mathrm{FS}) = \{r[1+\rho(f_T-2)]\}^{-1/2} \qquad (10)$$

$r(<1)$ is the COOH/OH ratio, ρ is the fraction of alcohol function belonging to T (here, no other polyol is present, thus $\rho = 1$) and f_T is the functionality of T ($f_T = 3$). In the present case, with binary systems, one simply has:

$$C_c(\mathrm{FS}) = (2r)^{-1/2} \qquad (11)$$

The different values of C_c(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)

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*), $C_c(Z)_{obs}$ 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[5–7] between P and T may be taken into account to explain that gap.

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 is 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*). In the ternary mixture, at 0.5 h C(Z) already reaches its highest level of 97% (*Figure 9*). As has been observed for P, 3% of COOH(Z) should be trapped too, but here free and monoesterified Z cannot be discriminated.

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

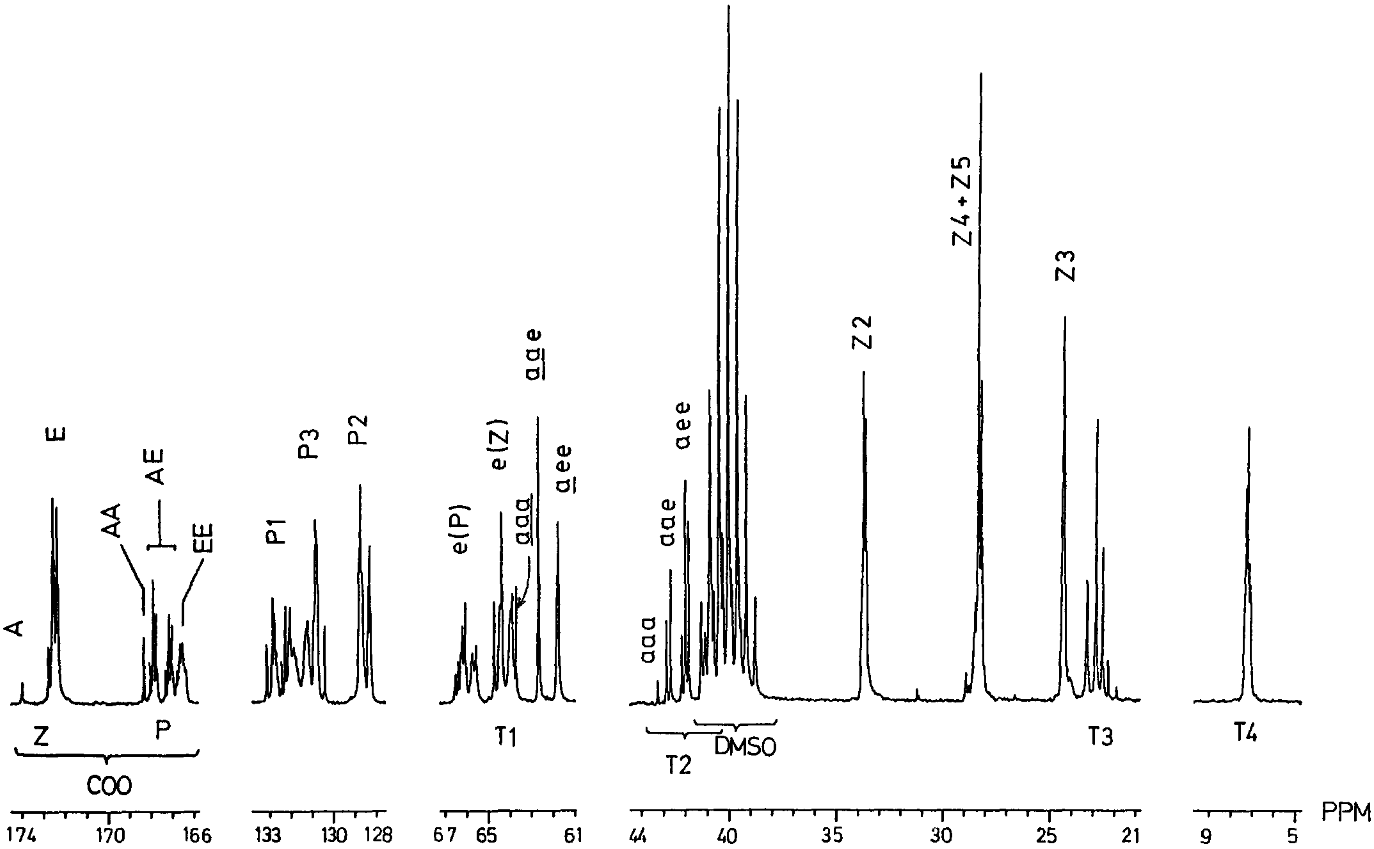


Figure 7 ^{13}C n.m.r. spectrum of a gelled copolyester of azelaic acid (Z, 0.5 mol)+*o*-phthalic anhydride (P, 0.5 mol)+trimethylolpropane (T, 0.8 mol) after 3.5 h at 180°C. Solvent, DMSO-d_6; temperature, 100°C. Conversions: COOH(Z)=96%; COOH(P)=63%; OH(T)=69%. A, E, a and e: see notes of *Figures 1* and *2* and text

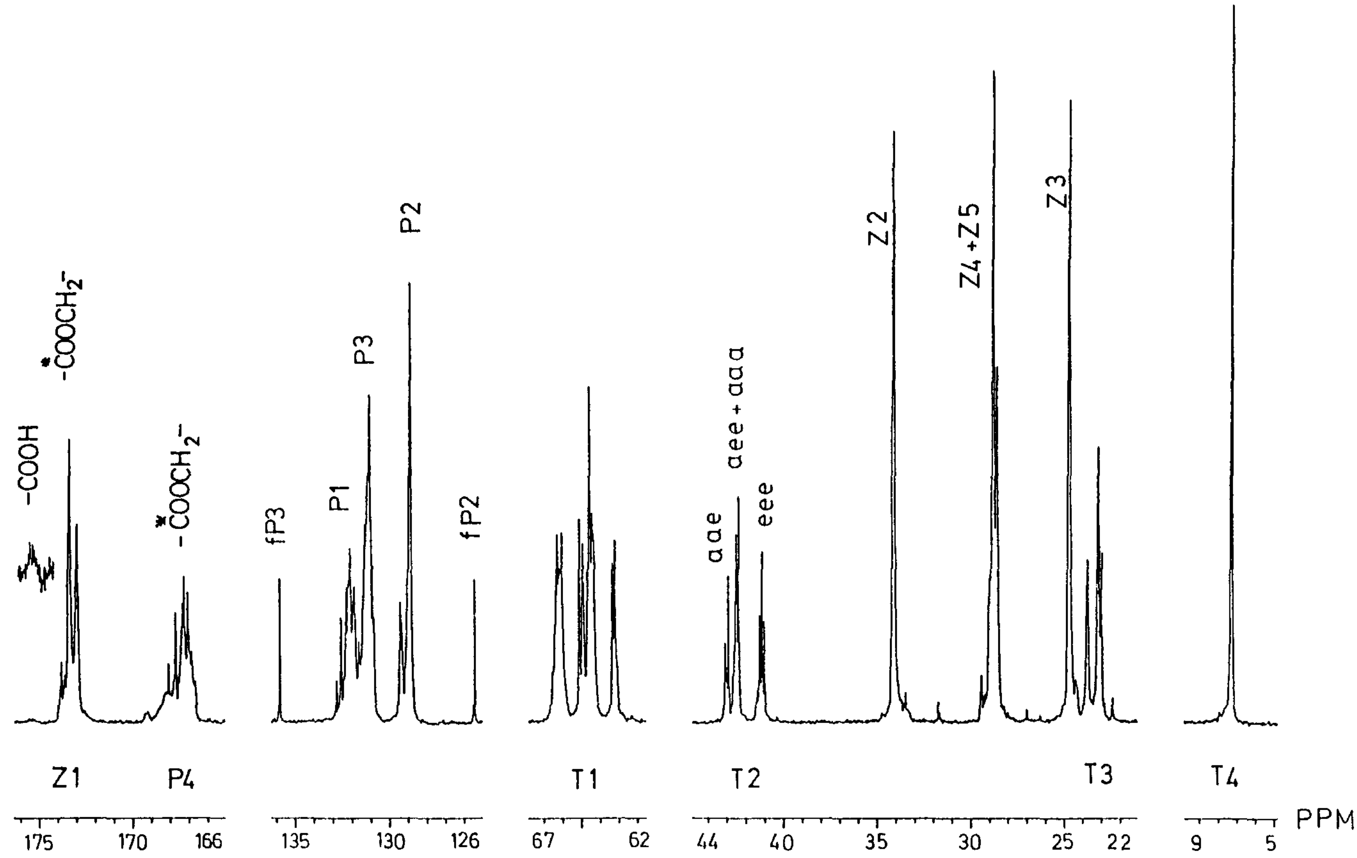


Figure 8 ^{13}C n.m.r. spectrum of a gelled copolyester of azelaic acid (Z, 0.5 mol) + *o*-phthalic anhydride (P, 0.5 mol) + trimethylolpropane (T, 0.8 mol) after 3.5 h at 180°C. Swollen gel in $CDCl_2$–$CDCl_2$; temperature, 100°C. Conversions: COOH(Z) = 97%, COOH(P) = 69%; OH(T) = 71%. fP_2, fP_3, carbons P_2 and P_3 of free *o*-phthalic anhydride. A, E, a, e: see notes of *Figures 1* and *4* and text

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 Ps have been shown and the T_2(eee) composite resonances may be quantitatively studied (*Figure 10b*).

Mechanisms of copolyesterification and statistical distributions of azelaic and phthalic branches on trimethylolpropane units

The more esterified the same T is by Z and/or P, the more its quaternary carbon T_2 resonances are shifted towards high fields. In TCE, the T_2 peak of traces of free T (identified by adding free T to the solution) at 43 ppm is hidden by the T_2(aae) resonances (42.7–43.3 ppm, *Figure 10b*). Here, T_2(aae) and T_2(aee) are less resolved than in DMSO, whereas T(eee) resonate in four overlapped peaks (40.8–41.8 ppm) that may easily be decomposed into four Lorentzian lines by simulation. Thus, the distributions of monoesters T(aae) and diesters T(aee) may be studied in DMSO (*Figure 10a*) and those of triesters T(eee) in TCE (*Figure 10b*). For simplicity, T monoesters, diesters and triesters are represented by (TP, TZ), (TPP, (TPZ + TZP), TZZ)

Table 3 Polyesterifications 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, $Cr(Acac)_3$; A and E, acid and ester groups of P; a and e, alcohol and ester groups of T

	1P + 0.8T	0.5P + 0.5Z + 0.8T	1Z + 0.8T
r = COOH/OH	0.83	0.83	0.83
Reaction time (h)	4	3.5	1.58
Sample	TP	TZP	TZ(IV)
Gel state	No	Covalent	Covalent
Conversions (%)			
alcohol (C(T))[a]	71	71	70
acid (C(Z))[b]	–	97 } 83^{e}	82
(C(P))[c]	82	69	–
acid (C_c(FS))[d]	77	77	77
Distributions (%) of P[f] and T[g]			
P(AA) (or P′)	2	5	–
P(AE)	33	49	–
P(EE)	65	46	–
T(aaa)	3	3	4
T(aae)	20	19	18
T(aee)	44	44	44
T(eee)	32	34	35

[a] Equations (2), (6), (7)
[b] Equation (1)
[c] Equation (8)
[d] Equations (10), (11)
[e] Obtained using 0.5(C(Z) + C(P))
[f] Equation (9)
[g] Equations (2)–(5)

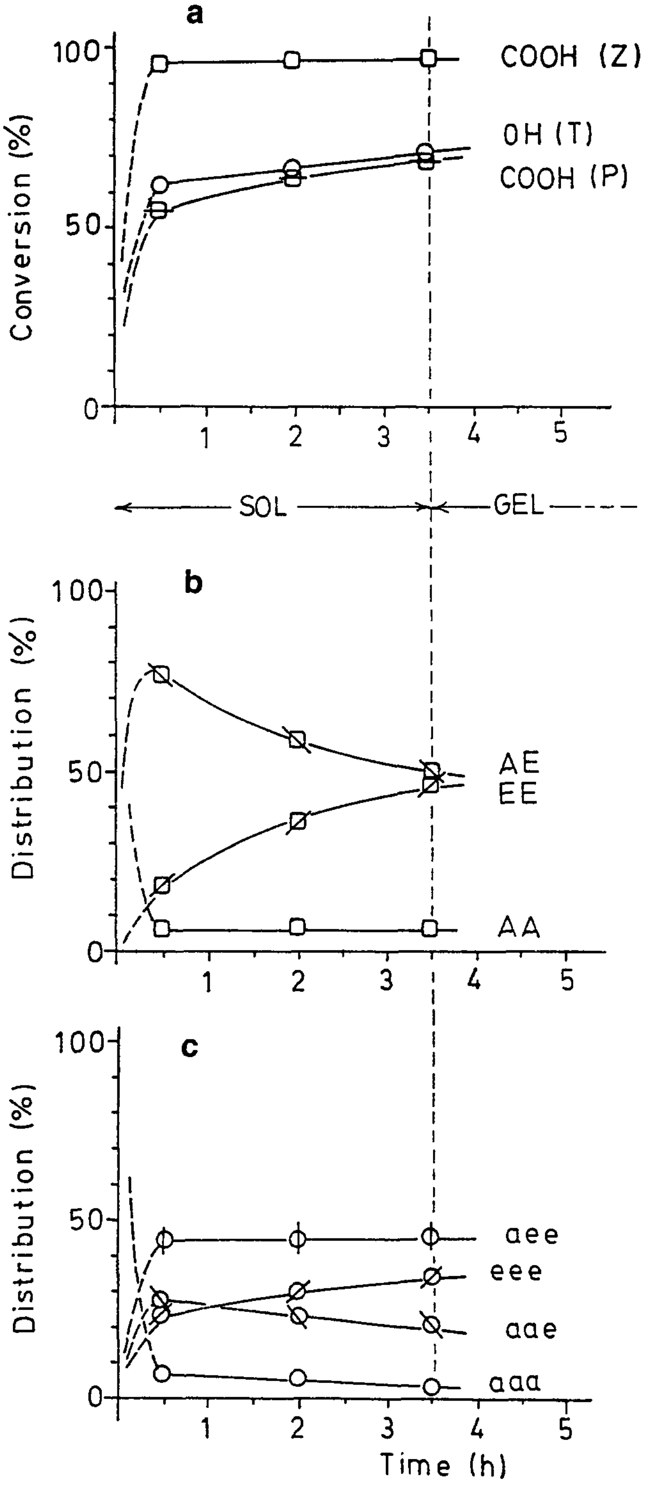


Figure 9 Copolyesterification of azelaic acid (Z, 0.5 mol), *o*-phthalic anhydride (P, 0.5 mol) and trimethylolpropane (T, 0.8 mol) in bulk at 180°C. Variations *versus* time. (a) Conversions of acid (Z, P) and alcohol (T). (b) Distributions of diesterified (EE), monoesterified (EA) and free P (AA).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

and (TPPP, (TPPZ+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:

$$p(P)=69/(97+69)=0.42$$

$$p(Z)=97/(97+69)=0.58$$

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:

$$p(P)=p(P/P)=p(P/Z)=0.43$$

$$p(Z)=p(Z/P)=p(Z/Z)=0.57$$

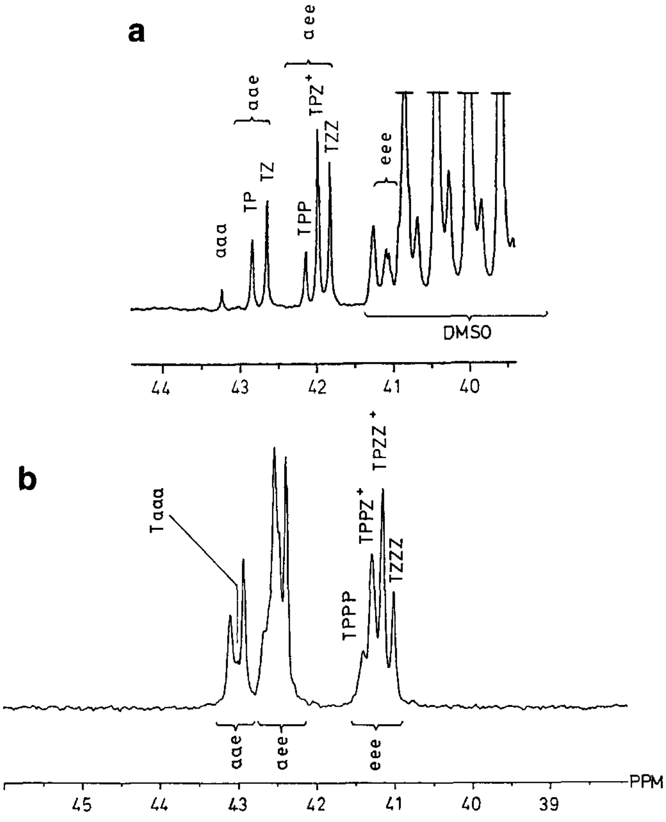


Figure 10 ^{13}C n.m.r. spectra of a gelled copolyester of azelaic acid (Z, 0.5 mol)+*o*-phthalic anhydride (P, 0.5 mol)+trimethylolpropane (T, 0.8 mol) after 3.5 h at 180°C. Swollen gel in DMSO-d_6 (a) and $CDCl_2$–$CDCl_2$ (b). Temperature, 100°C. Enlargement of the resonances of T quaternary carbons (40–44 ppm). TZ, TP, mono azelaate and *o*-phthalate of T; TZP, mixed diester (azelaate, *o*-phthalate) of T, etc.

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:

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

$$TPZ + TZP = TPZ^+$$

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

$$\begin{aligned} p(PP) &= p(P)p(P/P) = p(P)^2 && \text{for TPP} \\ p(PZ)^+ &= p(PZ) + p(ZP) \\ &= p(P)p(Z/P) + p(Z)p(P/Z) \\ &= 2p(P)p(Z) && \text{for } TPZ^+ \qquad (12) \\ p(ZZ) &= p(Z)p(Z/Z) = p(Z)^2 && \text{for TZZ} \end{aligned}$$

with

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

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 again assumed, one gets:

$$p(P/PP) = p(P/PZ) = p(P/ZP) = p(P/ZZ) = 0.43$$

$$p(Z/ZZ) = p(Z/PZ) = p(Z/ZP) = p(Z/PP) = 0.57$$

Thus:

$$\begin{aligned} p(PPP) &= p(P)^3 && \text{for TPPP} \\ p(PPZ)^+ &= 3[p(P)^2 p(Z)] && \text{for } TPPZ^+ \\ p(PZZ)^+ &= 3[p(P)p(Z)^2] && \text{for } TPZZ^+ \qquad (13) \\ p(ZZZ) &= p(Z)^3 && \text{for TZZZ} \end{aligned}$$

Table 4

Calculated probabilities of presence	Observed normalized intensities	$T_2(\delta, ppm)$ (in DMSO)	Diesters
$p(PP) = 0.185$	0.20	42.05	TPP
$p(PZ)^+ = 0.49$	0.49	41.89	TPZ^+
$p(ZZ) = 0.325$	0.31	41.74	TZZ

Table 5

Calculated probabilities of presence	Observed normalized intensities (simulation)	$T_2(\delta, ppm)$ (in TCE)	Triesters
$p(PPP) = 0.079$	0.07	41.41	TPPP
$p(PPZ)^+ = 0.316$	0.28	41.29	$TPPZ^+$
$p(PZZ)^+ = 0.419$	0.43	41.15	$TPZZ^+$
$p(ZZZ) = 0.185$	0.22	41.01	TZZZ

with

$$p(PPP) + p(PPZ)^+ + p(PZZ)^+ + p(ZZZ) = 1$$

The four calculated probabilities of presence allow the identification of the four Lorentzian peaks obtained by simulation of the T_2(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 pleads 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% × 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 $C(Z) = 82\%$ ($> C_c(FS) = 77\%$) at 1.58 h (*Table 3*), whereas only mobile solution is observed with $C(Z) = 79\%$. The actual critical conversion of COOH(Z) ($C_c(Z)$) 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:

$$TPPP < TPPZ < TPZZ < TZZZ$$

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) ≈ 34–35%.

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