Polyestereamide 6NT6: polycondensation kinetics, d.s.c. and n.m.r. studies of thermally treated samples

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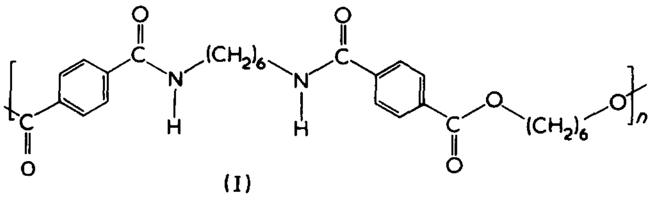
Samples of alternated polyestereamide (PEA) obtained after prolonged polycondensation were examined viscometrically and by differential scanning calorimetry. The intrinsic viscosities at different polycondensation times for various process parameters were determined. A phenomenological equation is proposed and used to determine the polycondensation and degradation kinetic parameters. D.s.c. of samples at different polycondensation times suggests that an extensive rearrangement of the alternated polymer takes place, leading to the formation of products having higher and lower melting points. Evidence and quantitative evaluation of these phenomena were obtained by means of ^{1}H and ^{13}C n.m.r. studies on samples purposely treated above their melting point. An interpretation based on an interchange reaction between ester and amide linkages is given.

INTRODUCTION

Among the alternated polyestereamides[1,2] (PEA) studied in our laboratories the following one:

PEA 6NT6:



(I)

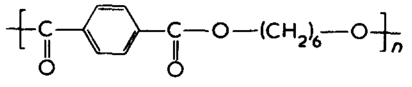
is particularly interesting as a synthetic fibre for its silk like handle and for its excellent dyeing properties.

The aim of this study is to explain the phenomena taking place during the polycondensation, and also when the polycondensation is taken beyond the time lag of practical interest (prolonged polycondensation). Our approach involves the study of simultaneous polycondensation and degradation kinetics of (I), the influence of polycondensation parameters and the characterization of the products obtained at different polycondensation times.

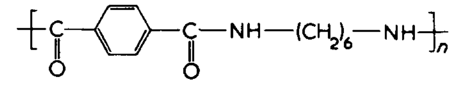
It is known[3,4] that by heating a mixture of two polyamides a transamidation reaction takes place with the formation of random copolymers. Moreover, an interchange reaction between ester and amide links for mixtures of polyester and polyamide has been reported[5].

In the case of a polyestereamide such as (I), a decrease in alternating units may be expected, coupled with the formation of polyamide (PA) and polyester (PE) sequences,

PE:



PA:



according to the Scheme 1:

$$2\text{–EA–} \rightarrow \text{–EE–} + \text{–AA–} \qquad (1)$$

where:

–EA– represents –HN–OC–ϕ–CO–O–;

–EE– represents –O–OC–ϕ–CO–O–;

–AA– represents –HN–OC–ϕ–CO–NH–.

In order to check this hypothesis, PEA samples from prolonged polycondensation and others, thermally treated above their melting point, were investigated.

EXPERIMENTAL

Polymerization

The polymer was obtained via transesterification and melt polycondensation of *N,N'*-bis(*p*-carbomethoxybenzoyl) hexamethylenediamine (DEA) with 1,6-hexanediol.

The catalyst used was titanium tetraisopropylate (0.02% mol/mol DEA). The commercial product (guaranteed reagent grade) was purified by distillation and used as a solution in isopropyl alcohol. Both polymerization phases (transesterification and polycondensation) were carried out in two different reactors in order to obtain different evaporating surface–polymer volume ratios (*S*/*V*). The evaporating surface and the volume were calculated assuming the polymer melt was at rest.

The reactors were: (a) a three-necked glass vessel with a

Table 1 Quantitative values derived from ^1H and ^{13}C n.m.r. spectra (t_f = 8 h)

Sample	T_f (°C)	$x_A(^1H)$	$x_A(^{13}C)$	x_{EA}	x_{AA}	x_{EE}
PEA	–	0.50	0.50	1.00	0.00	0.00
A	295	0.56	0.55	0.44	0.33	0.23
B	295	0.73	0.73	0.33	0.56	0.11
C	295	0.50	0.49	0.48	0.25	0.27
D	265	0.52	0.51	0.56	0.23	0.21

capacity of 0.5 and 1 l; (b) a 20 l cylindrical autoclave with conical bottom. Both reactors were equipped with a stirrer and take-off column.

The transesterification was carried out, under nitrogen with molar ratio hexanediol/DEA 2:1, at a variable temperature (165°–257°C) for the autoclave and at a constant temperature (240°C) for the glass vessel. The time required for transesterification was evaluated from the initial methanol distillation and taken to be the time required for the conversion reaction to reach 95% of that determined from the methanol output. This time changes as a function of the reactor employed due to the different heat capacity and heat transfer characteristics of the apparatus. It was 60 min for the autoclave and 30 min for the glass vessel. It was ascertained that these differences do not appreciably affect the following polycondensation. Polycondensations were carried out under variable pressure and temperature until a pressure, less than 1 Torr, and the prefixed polymerization temperature (265°–280°C), were reached.

In both polymerization phases, the melt was stirred continuously at 22 rev/min in the autoclave and at a variable speed, less than 22 rev/min, in the glass vessel.

As it was impossible to determine the polycondensation starting time, the time at which a pressure of less than 1 Torr was achieved in the reactor was assumed to be the initial point. At this moment, the distillation of hexanediol reached 80–93% of its final output. At any prefixed time polymer was drawn from the reactor by means of a glass tube.

Thermal treatments

Table 1 summarizes the various thermal treatments carried out. In a typical experiment, the polymer sample was dried at 130°C at 0.5 mmHg for 8 h and then maintained under an inert gas without stirring at a temperature T_f (always above the melting temperature of PEA) for a time t_f. In one case (sample A, with $T_f = 295°C$ and $t_f = 8$ h) an extraction at room temperature was carried out using a phenol–tetrachloroethane mixture, a good solvent for PEA. The insoluble (27%) and soluble fractions will be referred to as sample B and C, respectively. Polyestereamide without thermal treatment will be henceforth referred to as 'simple PEA'.

The model compounds for n.m.r. investigations were prepared as follows. Poly(hexamethylene terephthalate) (PE) was obtained from dimethyl terephthalate and 1,6-hexanediol via transesterification and melt–polycondensation using titanium tetraisopropylate as catalyst. *N,N'*-bis (6-aminohexane) terephthalamide (MAA) was obtained via transamidation of dimethyl terephthalate with 1,6 hexamethylenediamine using a toluene–methanol mixture as solvent and lithium methoxide as catalyst. The compound was purified according to the usual techniques.

Intrinsic viscosity

Intrinsic viscosity $[\eta]$ was determined at 25°C in phenol–tetrachloroethane (50/50 by wt) using a Ubbelohde viscosimeter.

Differential scanning calorimetry

D.s.c. measurements were carried out with a Du Pont 900 Thermal Analyser. A scan speed of 10°C/min was used. Glass beads were used as reference material. Melting points (T_m) were determined on powdered samples (~10 mg), in a sealed pan, crystallized for 10 min at temperatures of the maximum crystallization rates.

Nuclear magnetic resonance

^1H n.m.r. spectra were run at room temperature in CF_3COOD with TMS as reference on a HA-100 Varian spectrometer; ^{13}C n.m.r. spectra were run under the same conditions on a XL-100 Varian spectrometer operating in the pulsed Fourier transform (FT) mode. The FT conditions: $SW = 5000$ Hz; $AT = 0.8$ sec; $PD = 3$ sec; $PW = 20$ μsec (90° $PW = 51$ μsec); ensured the complete relaxation for carbon nuclei used in quantitative work (*Figure 8*). Otherwise (*Figure 7*) $PD = 0$ was used. Peak areas were obtained by means of the built-in electronic integrators of the spectrometers.

RESULTS AND DISCUSSION

Polycondensation kinetics

In *Figure 1a* the intrinsic viscosities $[\eta]$ *versus* the polycondensation time (t_p) at different values of S/V measured as described in the Experimental section, are shown. S/V strongly affects the maximum $[\eta]$ achieved during the polycondensation. The influence of polycondensation temperature (T_p) on the kinetics is plotted in *Figure 1b*. T_p strongly influences the polymer degradation.

Polycondensation and degradation kinetic parameters

Recently an attempt was made[6] to determine the rate parameters of polycondensation and degradation of β-bishydroxyethyl terephthalate. The mathematical models chosen by the author do not lead, in our case, to understandable results because the decrease of molecular weight does not follow the law assumed *a priori* by the author according to which the molecular weight decreases with the reciprocal of polycondensation time.

Following a suggestion found in the literature[7], we have used a mathematical expression which describes the kinetic curves represented in *Figure 1*, without an *a priori* knowledge of the polymer formation process. Plotting semilogarithmically $[\eta]$ *versus* t_p, the function, for high values of t_p, becomes a straight line with a slope equal to $-\omega/2.3$. This means that $[\eta] = [\eta]_0 \exp(-\omega t_p)$, for high values of t_p. The difference between $[\eta]_0 \exp(-\omega t_p)$ and $[\eta]$ plotted *versus* t_p can be also represented by a straight line with a slope $-\alpha/2.3$.

This means that we can express $[\eta]$ as:

$$[\eta] = [\eta]_0 [\exp(-\omega t_p) - \exp(-\alpha t_p)] \qquad (2)$$

This equation fits the behaviour of $[\eta]$ as a function of t_p very well as is shown in *Figure 2* where the curved line represents the function (2) while the points are the experimental values for the polycondensation kinetics. The

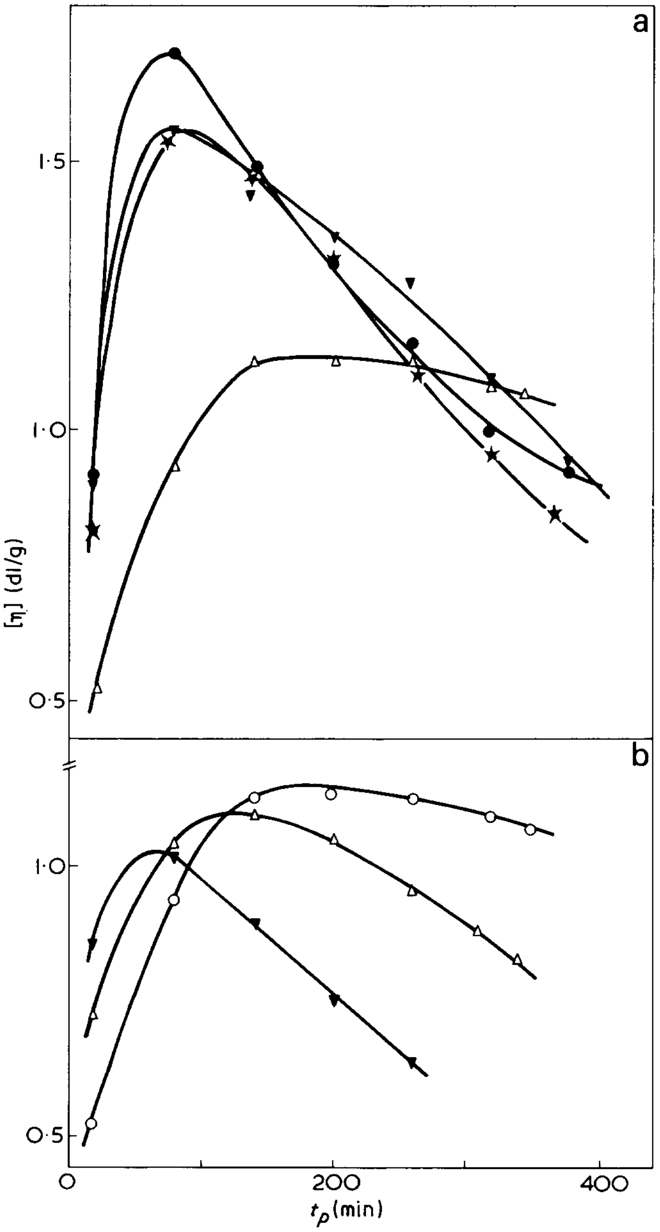


Figure 1 (a) Intrinsic viscosity at 25°C *versus* polycondensation time t_p plotted at different values of S/V and T_p = 265°C. S/V (dm^{-1}): ●, 7.95; ★, 5.76; ▲, 4.42; △, 1.12. (b) Intrinsic viscosity *versus* polycondensation time t_p plotted at different polycondensation temperatures T_p and S/V = 1.12 dm^{-1}. T_p (°C): ○, 265; △, 270; ▼, 280

straight lines were used to calculate the constants ω and α.

Equation (2) can easily be understood when it is rewritten in the following form:

$$[\eta] = [\eta]_0\{[1 - \exp(-\alpha t_p)] - [1 - \exp(-\omega t_p)]\} \quad (3)$$

In equation (3) the binomial $1 - \exp(-\alpha t_p)$ represents the increase of intrinsic viscosity in the absence of irreversible thermal degradation which is described by $-[1 - \exp(-\omega t_p)]$, a negative contribution to the intrinsic viscosity. α and ω represent kinetic parameters for the propagation and degradation kinetics, respectively and $[\eta]_0$ represents the maximum value of intrinsic viscosity achievable in the absence of degradation. In *Figure 3* α, ω and $[\eta]_0$ are plotted *versus* S/V.

These results demonstrate that in order to obtain a higher polycondensation rate and a higher molecular weight it is necessary to operate with reactors having a higher S/V ratio. The same situation happens in the case of poly (ethylene terephthalate) polycondensation although the proneness of this last polymer to thermal degradation is less critical.

Temperature effects on polymer structure

The melting temperature T_m of the polymer is a function of t_p; at first it falls and then increases. For a large value of t_p besides the main melt peak, two other peaks appear. One (T_{m2}) is lower, and the other (T_{m3}) is well above the polyestereamide main melt peak. Both T_{m2} and T_{m3} are t_p dependent in such a way that T_{m2} is decreasing and T_{m3} is increasing as t_p increases. In *Figure 4* T_{m3} *versus* t_p at different polycondensation temperatures T_p is shown. A typical development of the melting peaks together with the crystallization peaks for polymers sampled during the course of polycondensation is shown in *Figure 5*. For a high t_p there are two new crystallization peaks, indicating that a new polymer structure has been formed besides the previous one.

This behaviour supports the hypothesis that besides a decrease of molecular weight there exists a macromolecular rearrangement, due to an interchange reaction between ester and amide links, which brings about the formation of polymeric structures having higher and lower melting points than the alternated polyestereamide.

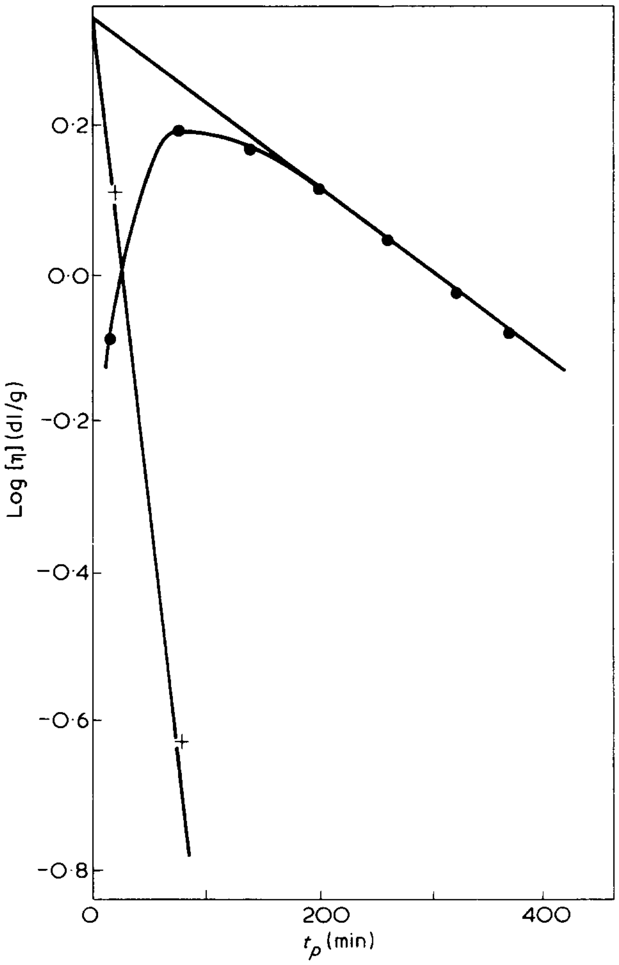


Figure 2 Log [η] plotted *versus* polycondensation time t_p

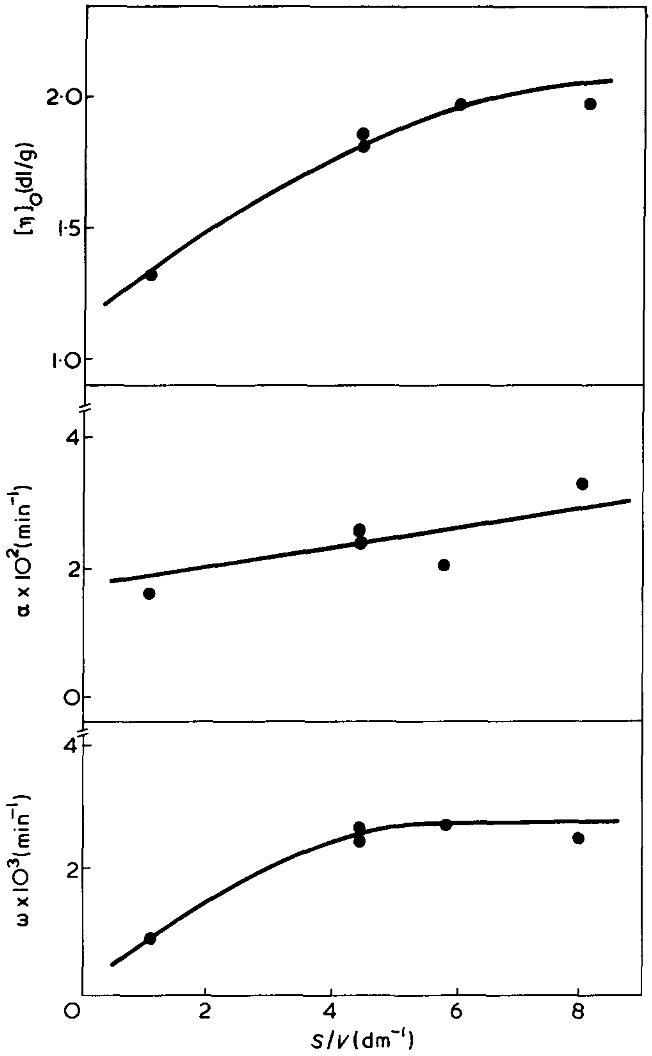


Figure 3 α, ω and $[\eta]_0$ plotted *versus S/V*

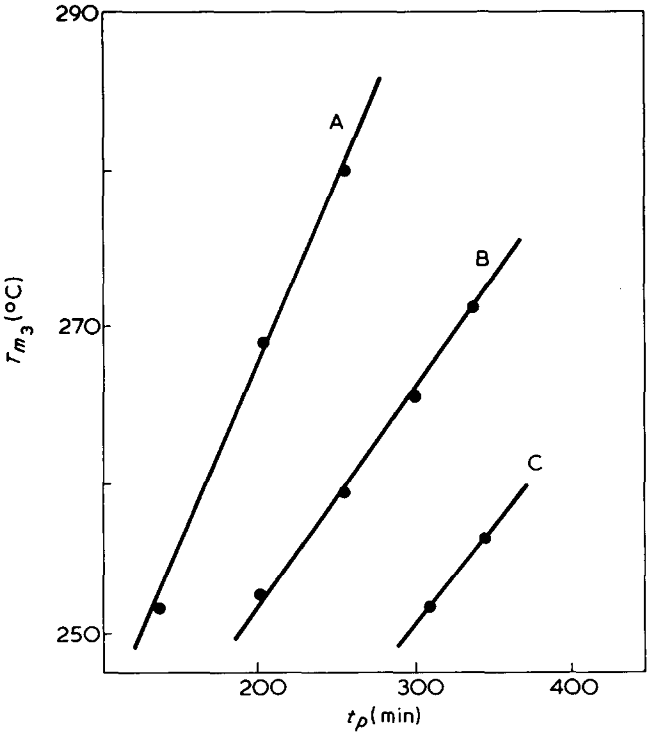


Figure 4 Transition temperatures T_{m3} plotted *versus* time at different polycondensation temperatures T_p (°C): A, 280; B, 270; C, 265

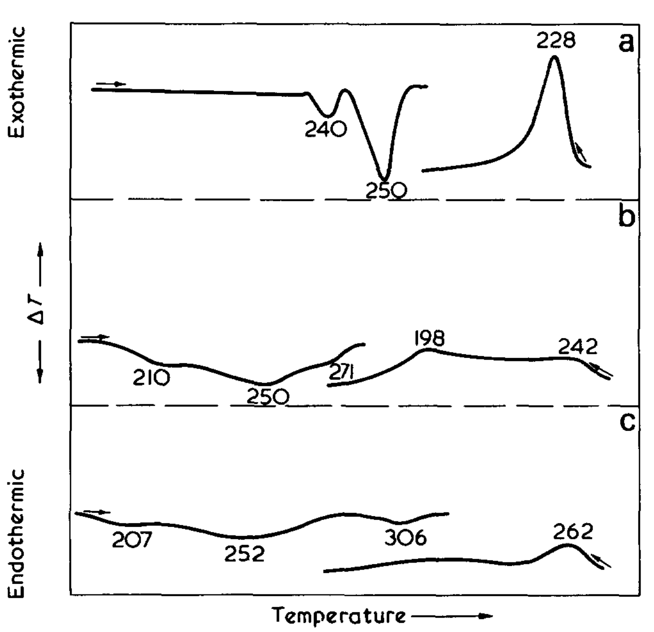


Figure 5 D.s.c. of three products at different polycondensation times: (a) t_p = 20 min; (b) t_p = 260 min; (c) t_p = 350 min. The arrows indicate: → heating, ← cooling; the numbers the temperature (°C)

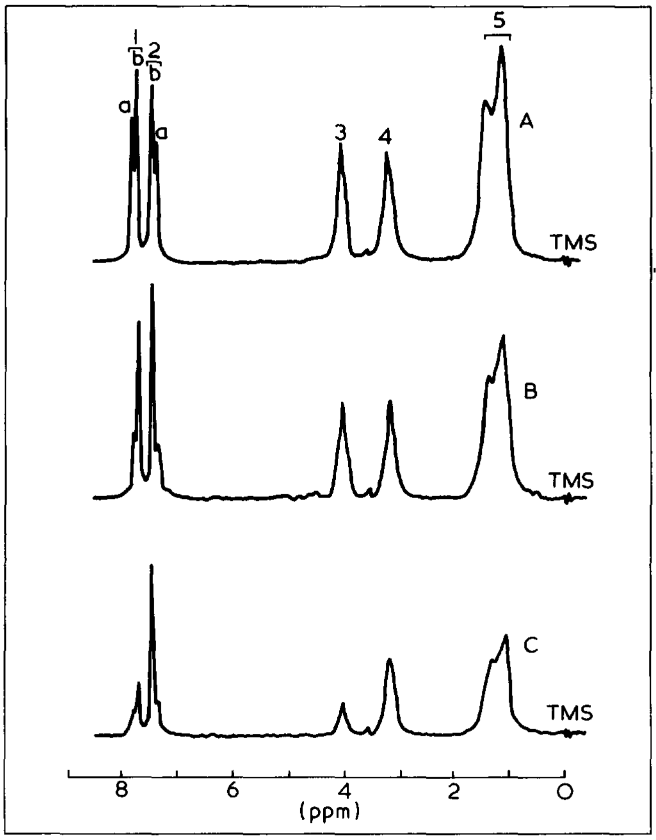


Figure 6 ^{1}H N.m.r. spectra of untreated (PEA) and thermally treated (A and B) samples of polyestereamide: A, PEA; B, sample A; C, sample B

^{1}H n.m.r. spectra

With the purpose of confirming this hypothesis, dried samples of polyestereamide were heated, in an inert atmosphere, at different temperatures for 8 h. The samples so obtained, whose d.s.c. thermograms show the same but more pronounced features as prolonged polycondensation ones, were analysed by means of n.m.r. techniques.

In *Figure 6* the ^{1}H n.m.r. spectra in CF_3COOD of PEA and samples A and B are reported. In the spectrum of simple PEA the AA′ BB′ pattern, characteristic of asymmetric *para*-disubstituted benzenes, is evident.

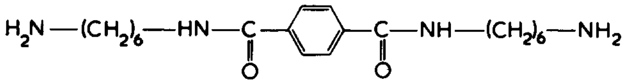
The mole fraction X_A (^{1}H) of amide groups, with respect to the total number of ester and amide groups, is obtained from the areas I_3 and I_4 of peaks 3 and 4 assigned to the methylene protons, neighbouring to the ester and amide group respectively, according to the expression:

$$X_A(^1H) = \frac{I_4}{I_3 + I_4}$$

The values so obtained are collected in *Table 1*.

For simple PEA X_A (^{1}H) = 0.50 is obtained, as expected from its regularly alternated structure. Thermally treated samples A and D show a moderate enrichment in amide group fraction. This enrichment, probably due to some degradation reaction of ester linkages, is not equally distributed over all polymer chains: in fact sample B, the fraction of A insoluble in phenol–tetrachloroethane, is very rich in amide groups while the corresponding soluble fraction C shows again $X_A(^1H)$ = 0.50. The spectra of A, C, D and, to an even greater extent, of B markedly differ from that of simple PEA: in fact the aromatic multiplets are modified by an intensity enhancement of internal peaks (b) compared to the external ones (a). In order to explain these facts, two model compounds, PE and MAA, representing respectively –EE– and –AA– sequences, were prepared and analysed by ^{1}H n.m.r.

MAA:



MAA was used as a model compound for polyamide groups because poly(hexamethylene terephthalamide) (PA) was found to be almost insoluble in trifluoroacetic acid.

The aromatic parts of the ^{1}H n.m.r. spectra of PE and MAA consist of singlets at chemical shifts identical to those of peaks marked 1b and 2b respectively in *Figure 6*. Therefore it is very likely that samples A, B, C and D contain, besides –EA–, also –EE– and –AA– sequences, which are absent in ordered, simple PEA. These facts support, although qualitatively, the ester–amide interchange reaction (Scheme 1).

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

For the purpose of this work, only carbonyl and aromatic carbon nuclei are significant. Therefore only the low field parts of spectra are discussed; moreover for simplicity, peaks due to the solvent CF_3COOD are omitted in *Figures 7* and *8* which represent the ^{13}C spectra of MAA, PE and PEA.

The symbolism used for the identification of the various carbons is the following: each carbon is given a number 1,2 or 3. If these numbers are indexed only on the top with symbols AA or EE (which stand for ‘amide–amide’ and ‘ester–ester’ linkages) they refer to –AA– and –EE– sequences respectively. For PEA, besides the top index EA (‘ester–amide’ linkages), a bottom index is required: A or E for carbons on the amide or ester side of the groups.

Assignments for MAA and PE are straightforward, based on chemical shifts and areas of peaks and are confirmed by undecoupled spectra.

In the case of PEA, two peaks for each type of carbon are observed, i.e. carbonyl, quaternary and unsubstituted aromatic. Although it seems reasonable to attribute the bottom index A to the peaks at chemical shifts closer to MAA peaks and, likewise, the bottom index E to the peaks at chemical shifts closer to PE peaks, an unambiguous proof of these hypotheses is difficult due to the small chemical shift differences involved. As will be clear shortly, however, for our purposes such assignments are not needed, it being only necessary to distinguish carbonyl from quaternary and unsubstituted aromatic peaks. This was carried out again with the aid of undecoupled spectra.

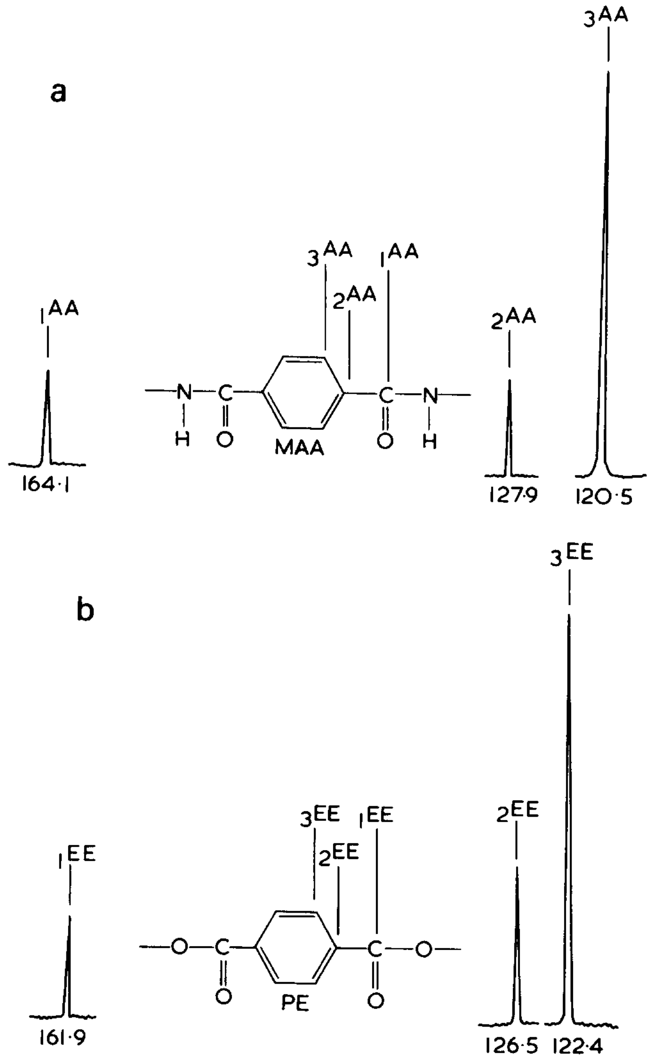


Figure 7 Low field part of ^{13}C n.m.r. spectra of model compounds (a) MAA and (b) PE. Chemical shifts (ppm) from TMS are given

^{13}C n.m.r. spectrum of sample A is shown in *Figure 8*. It is easily recognized that, besides PEA peaks, six additional peaks are present. Their chemical shifts agree with those found in the model compounds MAA and PE within 0.2 ppm. Therefore it can be concluded that not only –EA–, typical of PEA, but also –EE– and –AA– sequences are present in sample A. The spectra of samples B, C and D are quite similar to that of A, the only differences being in the areas of peaks.

An evaluation of the mole fractions X_{AA}, X_{EE} and X_{EA} of –AA–, –EE– and –EA– sequences and of X_A (^{13}C), which has the same meaning of X_A (^{1}H), is obtained from integration of peaks of type 3 carbons, best suited for this purpose:

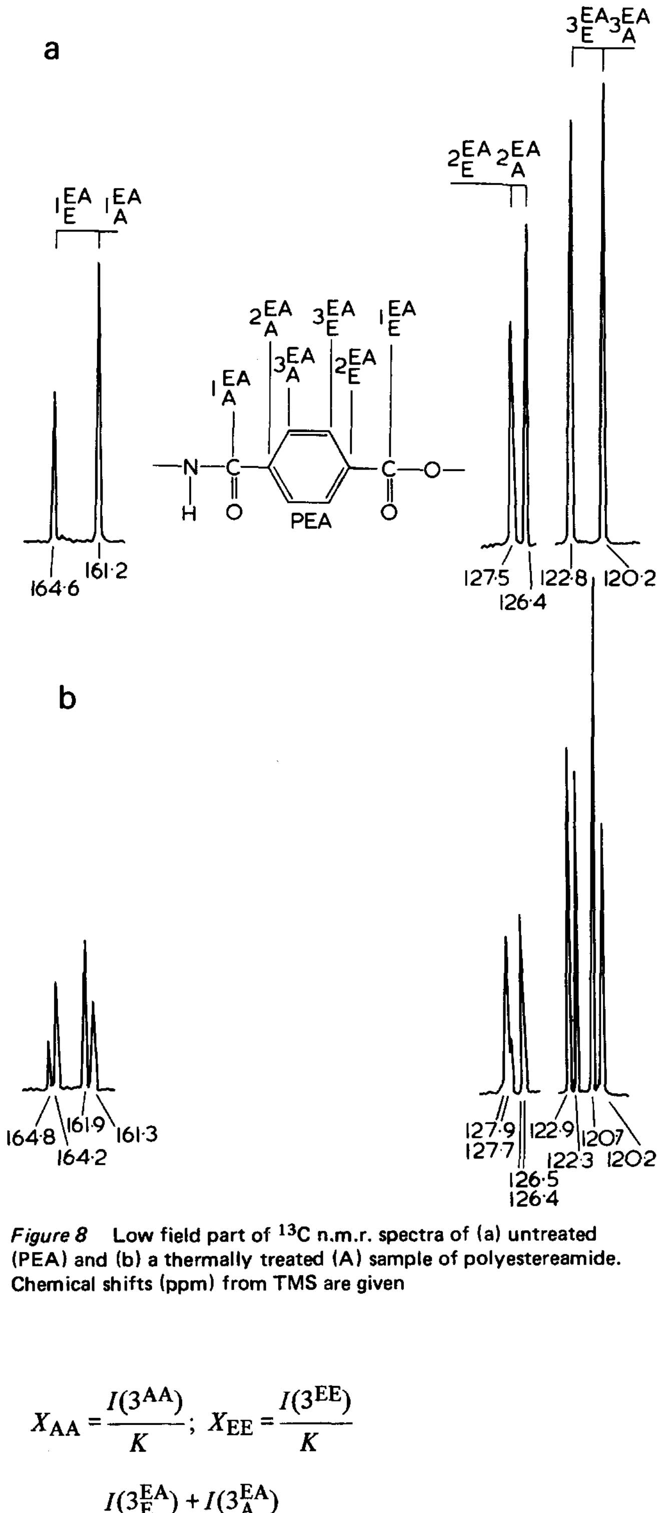


Figure 8 Low field part of ^{13}C n.m.r. spectra of (a) untreated (PEA) and (b) a thermally treated (A) sample of polyestereamide. Chemical shifts (ppm) from TMS are given

$$X_{AA} = \frac{I(3^{AA})}{K};\ X_{EE} = \frac{I(3^{EE})}{K}$$

$$X_{EA} = \frac{I(3_E^{EA}) + I(3_A^{EA})}{K}$$

$$X_A(^{13}C) = \frac{I(3_A^{EA}) + I(3^{AA})}{K}$$

where $K = I(3_A^{EA}) + I(3_E^{EA}) + I(3^{AA}) + I(3^{EE})$ and $I(i)$ are the peak areas. It is worth noting that $I(3_A^{EA})$ and $I(3_E^{EA})$ must be equal, as in fact was experimentally found. Results obtained for X_{AA}, X_{EE}, X_{EA} and $X_A(^{13}C)$ are given in *Table 1.* These data give a quantitative evaluation of the extent of the interchange reaction.

Experimental values of X_{EA}, X_{AA} and X_{EE} for all thermally treated samples are generally not very far from those expected for a random redistribution of amide and ester linkages, exceeding in the sense of a greater tendency to —AA— sequences for a heavy treatment.

The formation of crystalline amide sequences in thermally treated samples has been detected also by X-ray investigations[8,9] and is probably responsible for the low solubility of the polymer.

CONCLUSIONS

This work shows that the polycondensation and degradation kinetics of PEA are strongly influenced by the geometry of the polycondensation reactor and by the polycondensation temperature.

Moreover, if the polymer is maintained above its melting point for a long time then an extensive molecular rearrangement is produced, according to the ester–amide interchange reaction, with almost random redistribution of ester and amide linkages. Evidence for this process comes from the formation of compounds having higher and lower melting points than PEA and from the presence of –AA– and –EE– groups, absent in alternated PEA. Furthermore, with heavy thermal treatments a moderate enrichment of amide groups fraction occurs, probably due to partial degradation of ester linkages, and a tendency for the formation of polyamide blocks appears.

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REFERENCES

1 Capaccioli, T., Crosta, R. and Sorta, E. *Proc. 2nd Meeting Ital. Soc. Rheol. Siena* May 1973
2 Manzini, G., Crescenzi, V., Ciana, A., Ciceri, L., della Fortuna G. and Zotteri, L. *Eur. Polym. J.* 1973, **9**, 941
3 Flory, P. 'Principles of Polymer Chemistry', Cornell Univ. Press, Ithaca, New York, 1953
4 Champetier, G. *Ind. Plast. Mod.* 1963, **15**, 2
5 Korshak, V. V., Vinogradova, S. V., Teplyakov, M. M. and Chernomordik, Yu. A. *Proc. Acad. Sci. USSR Chem. Sect.* 1962, **147**, 1098
6 Tomita, K. *Polymer* 1973, **14**, 50
7 Sokolov, L. B. 'Synthesis of polymers by polycondensation', (Ed. I. P. S. T.), Jerusalem, 1968
8 Cesari, M., Perego, G. and Melis, A. *Eur. Polym. J.* 1976, **12**, 585
9 Perego, G. and Cesari, M. unpublished data