Transesterification reactions between a polyarylate and poly(1,4-butylene terephthalate): identification of interchange units via model compounds

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The reactions taking place during melt mixing of polyarylate (a copolyester of bisphenol A and an equimolar mixture of isophthalic and terephthalic acids) with poly(butylene terephthalate) (PBT) were studied by ^{1}H and ^{13}C nuclear magnetic resonance (n.m.r.). Model compounds whose structures match those of the polymers and possible interchange units were synthesized and characterized by ^{1}H and ^{13}C n.m.r. By means of this characterization, assignments of the absorptions appearing in the spectra of the soluble fraction were possible.

(Keywords: poly(1,4-butylene terephthalate); polyarylate; mixture; interchange reactions; model compounds; nuclear magnetic resonance)

INTRODUCTION

It is widely recognized that almost all polycondensates have polymer links that are easily cleaved or exchanged at processing temperatures. The mechanisms of the interchange reactions that occur in polyester blends during melt processing involve acidolysis, alcoholysis and/or direct transesterification. All these reactions result in the formation of new copolymers.

Devaux *et al.*[1] have shown that direct transesterification is the most likely mechanism of interchange reactions in blends of bisphenol A polycarbonate (PC) with poly(ethylene terephthalate) (PET) or poly(butylene terephthalate) (PBT). Kimura[2] has studied blends of polyarylate (PAr) and PBT using dynamic mechanical methods in order to monitor the reaction and determine its effect on crystallinity and phase behaviour.

I.r. and n.m.r. spectroscopies are preferred among the few direct and quantitative analysis methods, despite their relative lack of sensitivity at low reaction levels.

In a previous article[3], we established evidence of the transesterification reaction that takes place when a mixture of polyarylate (PAr), a copolyester of bisphenol A and an equimolar mixture of isophthalic and terephthalic acids, and poly(butylene terephthalate) (50/50) is heated up to 250°C for 240 min. We also reported an i.r. and n.m.r. study on the chloroform-soluble fraction that results from the thermal treatment of the initial polymers.

By studying the i.r. spectrum of this soluble fraction we were able to establish the existence of two different carbonyl groups as a consequence of the appearance of two absorptions: one at 1739 cm^{-1} due to the phthalic ester of bisphenol A and the other corresponding to the carbonyl group of PBT at 1720 cm^{-1}. Through the ^{1}H n.m.r. analysis (*Figure 1*) of the chloroform-soluble fraction (PBT is not soluble in chloroform), it was possible to confirm the incorporation of PBT units into the soluble fraction, as can be observed by the band appearing at 8.10 ppm, and the generation of a new unsymmetrically disubstituted terephthalic ester unit that appears at 8.25 and 8.17 ppm. Moreover, we were also able to observe other low-intensity absorptions that might be due to the formation of other interchange units whose structures *a priori* were difficult to identify.

In a great number of cases n.m.r. studies of vinyl polymers as well as polycondensates have met with high success through the synthesis and characterization of low-molecular-weight species that contain in their structures those functional groups which are the repeat units of the polymeric chain; these molecules are usually called model compounds.

Thus, in order to study stereochemical configurations of vinyl polymers, n.m.r. analysis of 2,4-disubstituted pentane isomers and 2,4,6-trisubstituted heptane isomers has often been applied. These compounds are the basic structure of both meso and racemic diads and iso-, hetero- or syndiotactic triads of polymers respectively. In this way, several polymers have been studied, such as polyacrylates[4,5], poly(alkyl vinyl ethers)[6,7], polyacrylonitrile[8], poly(vinyl chloride)[9–11] and polystyrene[12–15], among others. In relation to polycondensates, Devaux *et al.*[16], by studying the reactions that take place between PC and two model compounds of PAr, illustrated interchange reactions between PC and PAr. Hvilsted[17] synthesized model compounds in order to determine the structures of multicomponent polyesters by means of their ^{13}C n.m.r. spectra.

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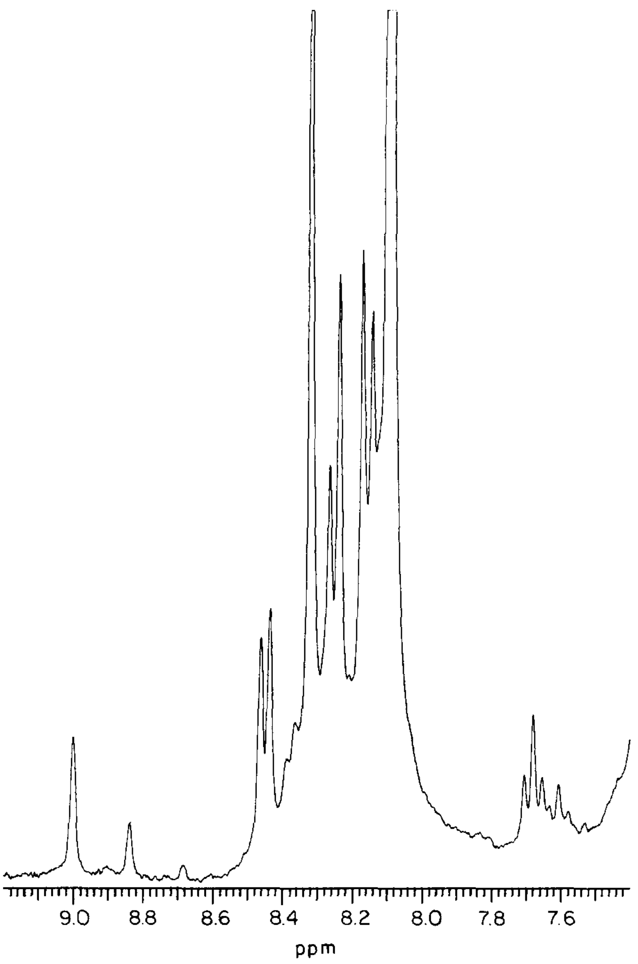


Figure 1 Aromatic part of ^{1}H n.m.r. spectrum of soluble fraction (enhanced)

In this paper, we present direct evidence of the interchange reaction between PAr and PBT. We base our evidence on n.m.r. experiments on the soluble fraction itself and on model compounds representing the polymer structures and the interchange units. We try to make a complete assignment of all absorptions present in the spectrum of the soluble fraction.

EXPERIMENTAL

Polymer purification, mixture preparation and experimental conditions of the thermal treatment reaction have been described elsewhere[3].

Preparation and purification of reagents

Commercially available dichlorides (Aldrich >99%) were distilled under vacuum to obtain colourless products, which were kept under N_2 at -20°C until use. 1-Butanol (Aldrich 99.4%) and 4-cumylphenol (Aldrich 99%) were used without further treatment.

Synthesis of model compounds

Isophthalic and terephthalic esters of 4-cumylphenol. First, 10 g (0.047 mol) of 4-cumylphenol and 4.77 g (0.023 mol) of terephthaloyl chloride (or iso-) were added to 30 ml of anhydrous pyridine. The mixture was refluxed in an inert atmosphere while being stirred for 90 min. After cooling, it was poured into a NaOH (50 ml, 10%) solution and shaken with chloroform. The organic phase was shaken three times with NaOH (10%) and HCl (10%), washed with a bicarbonate solution and finally with distilled water to neutral pH. The solvent was evaporated and the residue was submitted to column chromatography on silica gel. (M.p. of 4-cumylphenol isophthalate, 138°C; m.p. of 4-cumylphenol terephthalate, 194°C).

Isophthalic and terephthalic esters of 1-butanol. The reaction conditions, molar ratio and product purification methods were the same as those described above. In these cases the reaction time was 5 h. Yellow oils were obtained.

Asymmetric isophthalates and terephthalates. The reaction conditions and product purification methods were the same as those already described. Molar ratio phenol/alcohol/phthaloyl chloride was 1:1:2 and the reaction time was 5 h. (M.p. of asymmetric isophthalate, 60°C; m.p. of asymmetric terephthalate, 69°C.)

4-Cumylphenyl monoterephthalate and monoisophthalate. A solution of cumylphenol (2 g, 9.42×10^{-3} mol) in anhydrous pyridine (20 ml) was added dropwise to a refluxed solution of terephthaloyl chloride (or iso-) (9.13 g, 0.094 mol) in anhydrous pyridine (60 ml) under N_2 while being stirred, and the reaction was kept for 2 h under these conditions. After cooling, the reaction mixture was precipitated into a NaOH (100 ml, 10%) solution, neutralized and extracted with chloroform. The organic phase was shaken three times with HCl (10%), and finally, washed with distilled water to neutral pH. The solvent was evaporated and the residue was submitted to column chromatography on silica gel. (M.p. of 4-cumylphenyl monoterephthalate, 217°C; m.p. of 4-cumylphenyl monoisophthalate, 158°C.)

Instrumentation

Proton and carbon nuclear magnetic resonance spectroscopy. The n.m.r. spectra were registered in a Varian VXR 300 spectrometer in deuterated chloroform at 20°C except for the case of PBT whose spectrum was registered in trifluoroacetic acid (TFAA)/$CDCl_3$; tetramethylsilane (TMS) was used as internal reference.

^{1}H n.m.r. (300 MHz) spectra were registered in 5 mm i.d. tubes in 10% w/v solutions with a spectral width of 4000 Hz, flip angle 90° and acquisition time 3.7 s. 16K data points were used for Fourier transform.

^{13}C n.m.r. (75.4 MHz) spectra were registered in 5 mm i.d. tubes in 20% solutions with a spectral width of 16000 Hz, flip angle 90°, delay 2 s and acquisition time 0.9 s. 32K data points were used for Fourier transform.

RESULTS AND DISCUSSION

The model compounds representing those polymeric structures under study are shown in *Figure 2*. Thus, I.a is a PBT model compound, whereas a I.b and I.c mixture would be representative of PAr. The interchange units that can be obtained after the reaction has taken place are represented by the model compounds II.a, II.b and II.c respectively. Thus, while compound II.a represents the resulting structure of the transesterification reaction between PAr's terephthalic units and PBT, compound II.b would be the reaction product of PBT and PAr's isophthalic units, and II.c would be the product of a double transesterification of the isophthalic units.

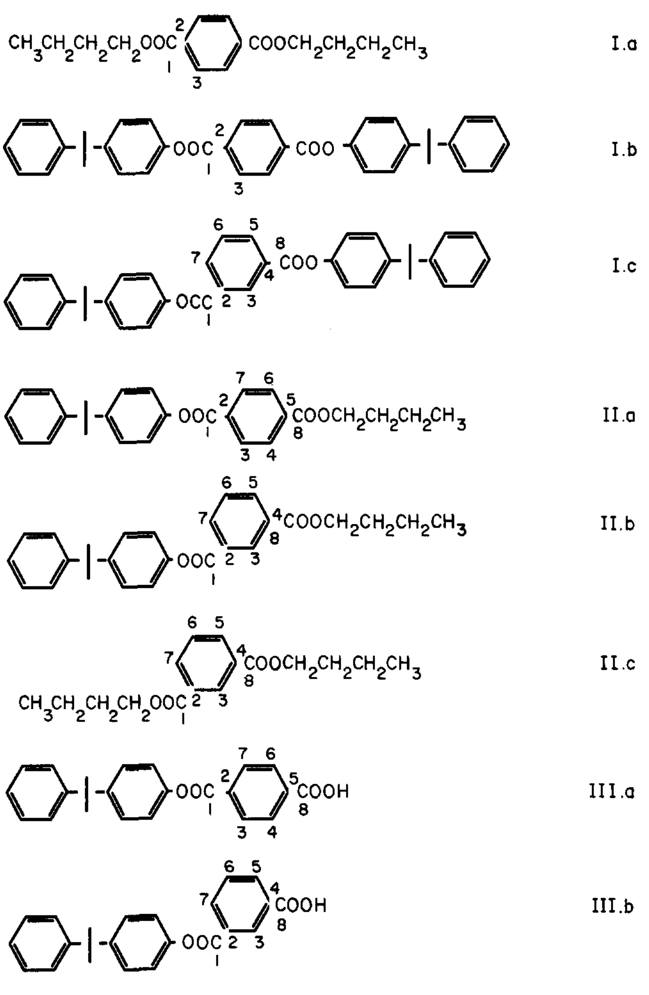


Figure 2 Formulae of the model compounds

N.m.r. spectra: introduction

In describing the spectra of all model compounds we will only refer to the tere- and isophthalic units; the rest of the absorptions will not be considered as they are not of interest in the reactions under study. To facilitate the interpretation of the spectra we have numbered each carbon of the tere- and isophthalic units. In addition, we want to point out that the numbers given to the protons refer to the numbers of the carbons to which they are attached.

N.m.r. spectra of model compounds of original units

Model compounds I.a and I.b. The ^1H spectra (*Figures 3a* and *3b*) of these compounds, as expected, show a unique signal corresponding in both structures to four magnetically equivalent protons at 8.10 (I.a.) and 8.31 ppm (I.b) respectively.

In the same way, the ^{13}C n.m.r. spectra (*Figures 4a* and *4b*) only show three absorptions for each structure, due to the three different carbons.

The chemical shifts are summarized in *Tables 1* and *2*.

Model compound I.c. In this structure three different types of protons can be distinguished, H3, H5(7) and H6, which give rise to an AM_2X system. The most unshielded proton H3 is located at 8.99 ppm as a split triplet. The magnetically equivalent protons H5 and H7 (8.44 ppm) appear as a double doublet coupled with protons H6 and H3, and proton H6 appears (7.67 ppm) as a split triplet (*Figure 3c*).

The analysis of the registered spectrum together with that obtained by means of simulation (LAOCOON3) allowed us to calculate the following coupling constants: $J_{3,5} = 1.74$, $J_{3,6} = 0.40$ and $J_{5,6} = 7.81$ Hz.

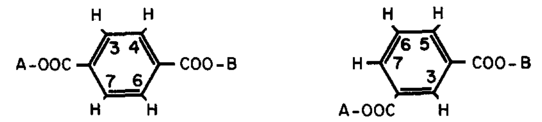
In the ^{13}C n.m.r. spectrum (*Figure 4c*) five signals can be observed: at 130.30 ppm due to the quaternary aromatic carbons C2 and C4; at 131.69 ppm, C3; at 129.02 ppm, C6; at 134.86 ppm, C5 and C7; and at 164.29 ppm, C1 and C8.

N.m.r. spectra of model compounds of interchange units

Model compound II.a. An asymmetric disubstitution produces remarkable differences in n.m.r. spectra compared with those of symmetrically substituted compounds. Thus, in the ^1H spectrum of this model compound, the characteristic absorptions of an AA'BB' system can be observed as a complex signal centred at 8.21 ppm, that is to say between the corresponding signals of the symmetrically substituted aromatic protons (*Figure 3d*). Spectrum simulation (LAOCOON3) allowed us to make the following assignments: $J_{3,7} = 2.07, J_{3,4} = 8.44, J_{3,6} = 0.38$ and $J_{4,6} = 1.38$ Hz.

In the ^{13}C spectrum (*Figure 4d*), the more relevant features are the appearance of six clearly separated signals due to the six different carbons in the structure. So, quaternary aromatic carbons are located at 134.76 and 133.26 ppm, this last one being adjacent to the carbonyl group of the aromatic ester. The carbons in *ortho* position to the carbons attached to the carbonyl groups absorb at 129.87 and 130.05 ppm. In this case, the carbon absorbing at higher fields is *ortho* to the aliphatic ester group C4–6. The two carbonyls are located at 164.45 ppm (aromatic ester C1) and 165.72 ppm (aliphatic ester C8).

Table 1 Chemical shifts of aromatic protons of model compounds, polymers and soluble fraction



		Chemical shift δ (ppm)					
A,B	Compound	H3,7	H4,6	H3	H5	H6	H7
A = B = R	PBT	8.17	8.17				
	I.a	8.10	8.10				
	II.c			8.69	8.23	7.53	8.23
	Sol.fr.	8.10	8.10	8.68	*	7.53	*
A = B = Ar	PAr[a]	8.32	8.32				
	I.b	8.31	8.31				
	PAr[b]			9.00	8.45	7.68	8.45
	I.c			8.99	8.44	7.67	8.44
	Sol.fr.	8.33	8.33	9.00	8.45	7.68	8.45
A = Ar, B = R	II.a	8.25	8.16				
	II.b			8.84	8.30	7.60	8.36
	Sol.fr.	8.26	8.17	8.84	*	7.60	8.38
A = Ar, B = H	III.a	8.31	8.25				
	III.b			8.93	8.38	8.44	7.66
	Sol.fr.	–	–	8.92	–	–	–

[a] Chemical shifts of terephthalic units
[b] Chemical shifts of isophthalic units
*Overlapped signals

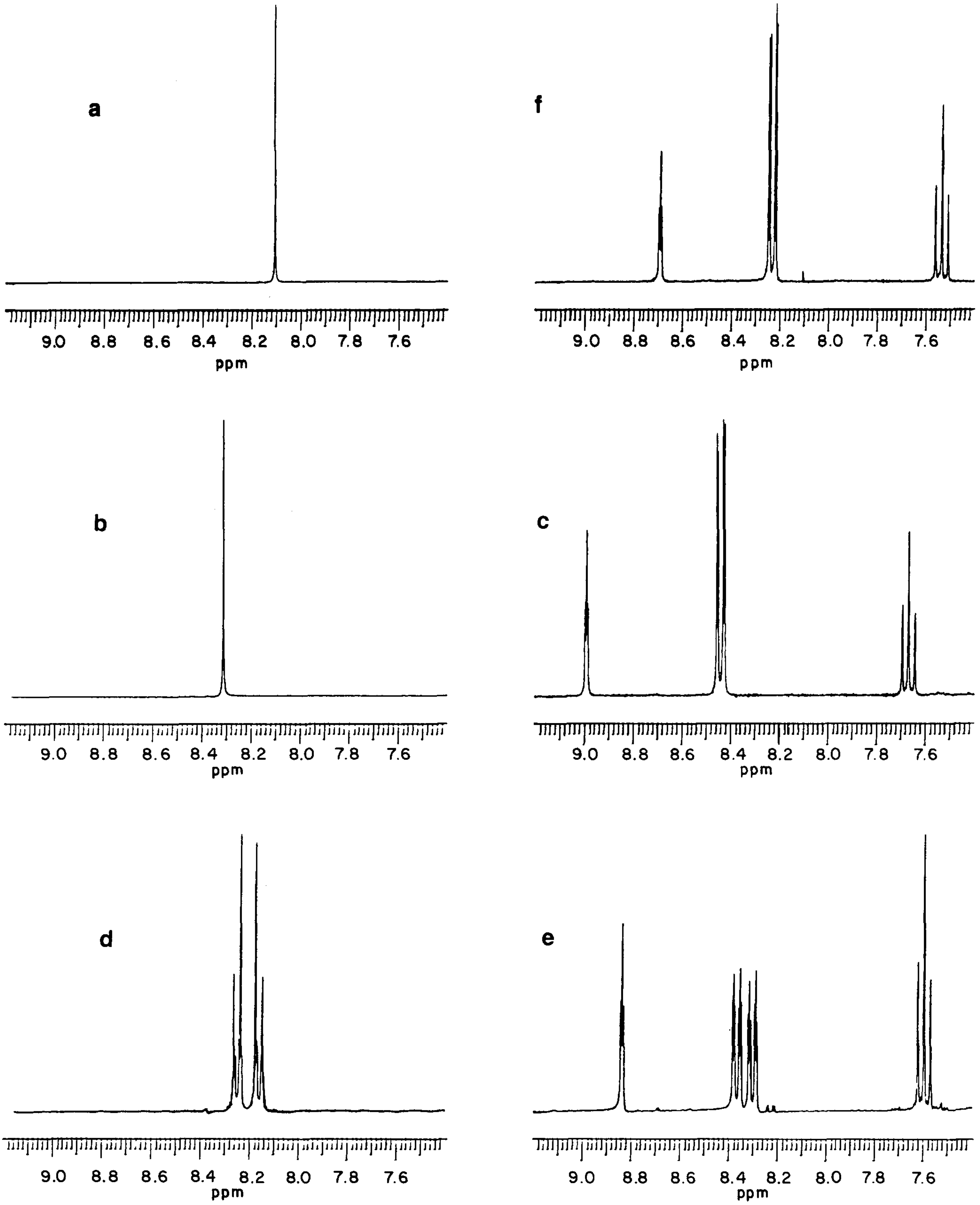


Figure 3 Terephthalic and isophthalic parts of ^1H n.m.r. spectra of model compounds: (a), (b) and (d) terephthalic model compounds I.a, I.b and II.a respectively; (c), (e) and (f) isophthalic model compounds I.c, II.b and II.c respectively

Model compound II.b. The ^1H spectrum (*Figure 3e*) shows an AMRX system with four non-equivalent protons. Unlike what we have mentioned about compound I.c, here protons H5 and H7 show clearly separated absorptions. H3 absorbs at 8.84 ppm as a split triplet because of the similarity of coupling constants $J_{3,5}$ and $J_{3,7}$. However, H5 and H7 appear as a double triplet at 8.30 and 8.36 ppm respectively. H6, the most shielded proton, is located at 7.60 ppm as a split triplet. $J_{6,5} \approx J_{6,7} = 7.82$, $J_{6,3} = 0.45$, $J_{5,7} \approx J_{5,3} \approx J_{7,3} = 1.51$ Hz.

The ^{13}C spectrum (*Figure 4e*) shows seven absorptions corresponding to the isophthalic carbons. The quaternary carbons appear at 130.04 ppm; C3 at 131.15 ppm and

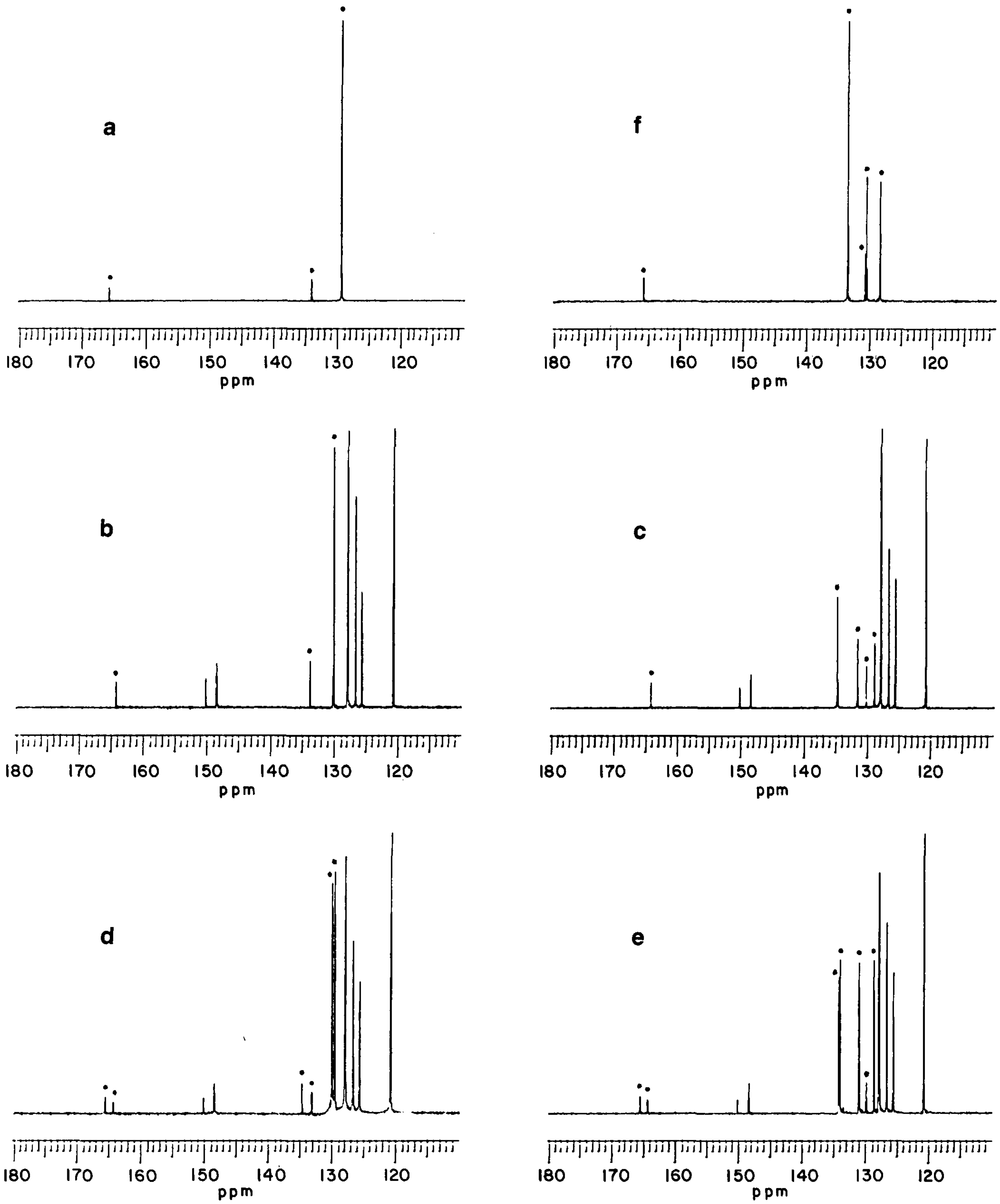


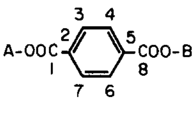
Figure 4 Terephthalic and isophthalic parts of ^{13}C n.m.r. spectra of model compounds: (a), (b) and (d) terephthalic model compounds I.a, I.b and II.a respectively; (c), (e) and (f) isophthalic model compounds I.c, II.b and II.c respectively. The signals corresponding to iso- and terephthalic carbons are marked with a dot

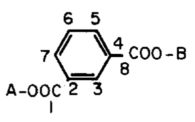
C6 at 128.78 ppm. C5 and C7 are well resolved and appear at 134.20 and 134.35 ppm respectively.

Model compound II.c. As in the case of model compound I.c, the ^{1}H spectrum (*Figure 3f*) shows absorptions at 8.69 ppm due to H3 appearing as a split triplet, H5(7) (magnetically equivalent in this structure) appear as a double doublet centred at 8.23 ppm and H6 appears at 7.53 ppm as a split triplet.

Five signals can be observed in the ^{13}C spectrum (*Figure 4f*): at 130.56 ppm due to quaternary carbons, at 130.84 ppm due to C3, at 133.60 ppm due to C5(7),

Table 2 Chemical shifts of isophthalic and terephthalic carbons of model compounds, polymers and soluble fraction





		Chemical shifts δ (ppm)							
A,B	Compound	C1	C2	C3	C4	C5	C6	C7	C8
Terephthalic units									
A = B = R	I.a	165.82	134.10	129.40	129.40	134.10	129.40	129.40	165.82
	PBT	168.49	133.98	130.48	130.48	133.98	130.48	130.48	168.49
	Sol.fr.	165.68	133.97	129.53	129.53	133.97	129.53	129.53	165.68
A = B = Ar	I.b	164.33	133.88	130.21	130.21	133.88	130.21	130.21	164.33
	PAr	164.31	133.89	130.23	130.23	133.89	130.23	130.23	164.31
	Sol.fr.	164.31	133.89	130.24	130.24	133.89	130.24	130.24	164.31
A = Ar, B = R	II.a	164.45	133.26	130.05	129.87	134.76	129.87	130.05	165.72
	Sol.fr.	*	133.40	130.11	129.65	*	129.65	130.11	*
Isophthalic units									
A = B = R	II.c	165.83	130.56	130.84	130.56	133.60	128.47	133.60	165.83
	Sol.fr.	–	–	–	–	–	–	–	–
A = B = Ar	I.c	164.29	130.30	131.69	130.30	134.86	129.02	134.86	164.29
	PAr	164.31	130.29	131.71	130.29	134.89	129.01	134.89	164.31
	Sol.fr.	164.31	*	131.72	*	134.89	129.05	134.89	164.31
A = Ar, B = R	II.b	164.47	130.04	131.15	130.04	134.20	128.78	134.35	165.70
	Sol.fr.	*	*	131.20	*	134.35	128.86	134.45	*

*Overlapped signals

at 128.47 ppm due to C6 and at 165.83 ppm due to carbons of the carbonyl group.

Discussion of soluble fraction spectra

Chemical shifts of the terephthalic and isophthalic protons of PBT, PAr together with those protons of the soluble fraction and model compounds are summarized in *Table 1*. If we fix our attention on the symmetrically *para*-disubstituted aromatic ring, it is worth pointing out that the coincidence in the chemical shifts of protons of PBT, bisphenol A terephthalate units and model compounds I.a and I.b is almost total, except in the case of PBT aromatic protons as they appear at higher fields owing to the solvent used in the registration of the spectrum ($CDCl_3$/TFAA-d_1). This coincidence is also observed in the case of protons of the symmetrically *meta*-disubstituted aromatic ring of bisphenol A isophthalate units and those of model compound I.c.

By observing even the very low-intensity absorptions in the ^1H spectrum of the soluble fraction (*Figure 1*), it is possible, at least in a tentative way, to assign these absorptions to structures similar to those of model compounds because the coincidence of chemical shifts of the different protons is almost total. However, the spectra of the model compounds are clearly more highly resolved than those of polymers, and, as a consequence of this high resolution, it is possible to observe coupling systems not perceptible in the case of the soluble fraction. The spectrum of model compound II.a shows the characteristic absorptions of an AA′BB′ system in the same positions as those of the interchange units of the soluble fraction, where only an AB system can be observed. Furthermore,

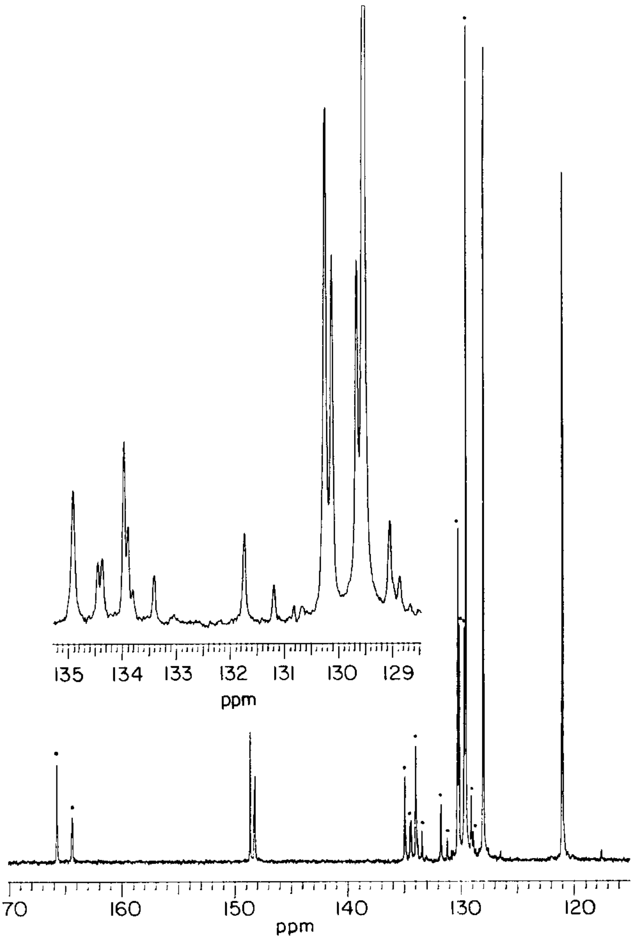


Figure 5 Isophthalic and terephthalic parts of ^{13}C n.m.r. spectrum of soluble fraction. The signals corresponding to iso- and terephthalic carbons are marked with a dot

when the substitution is asymmetric, as is the case of model compound II.b, we observe that all its signals are present in the spectrum of the soluble fraction, but it is worth pointing out that one of the signals of protons H5 and H7 is superimposed on the absorption of the symmetric *para*-disubstituted aromatic protons of PAr, and the other part of the signal is found at the beginning of the same absorption.

Moreover, the spectrum of the soluble fraction presents some weak absorptions at 8.68 and 7.54 ppm, which coincide with those of model compound II.c. In other words, these absorptions will correspond to a double aliphatic substituted isophthalic ring structure. However, we must stress that the extent of the reaction is extremely low. In addition to these weak absorptions, the very low absorption at 8.92 ppm, which is not always observed in the spectrum of the soluble fraction, does not have any correspondence with the structures of the model compounds described so far. Its chemical shift would be in accordance with a structure in which hydrolysis of the ester group would have taken place, yielding a chain with a terminal carboxylic acid group. In order to confirm this hypothesis, we have synthesized the model compounds whose structures are presented in *Figure 2*.

From the ^{1}H spectra of these model compounds we may conclude that even though the chemical shift (8.92 ppm) coincides with that of the proton *ortho* (model compound III.b) to the carboxylic acid as well as to the aromatic ester, the rest of the absorptions of these compounds are not observed in the ^{1}H spectrum of the soluble fraction.

In relation to the ^{13}C spectrum of the soluble fraction (*Figure 5*), we can confirm the presence of absorptions corresponding to both the terephthalic carbons of PBT and the interchange units where an asymmetric disubstitution in *para* or *meta* positions of the aromatic ring has taken place. However, there is no further contribution to what we have already established through the study of the ^{1}H spectra.

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