PII: S0032-3861(96)00754-9

Polymer Vol. 38 No. 9, pp. 2033–2039, 1997
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0032-3861/97/$17.00 + 0.00

^{1}H n.m.r. study on the ring opening selectivity of aromatic dianhydrides towards methanol

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(Received 19 June 1995)

Several isomeric aromatic diester-diacids may appear as a result of the opening selectivity of anhydride groups towards the alcohol. ^{1}H n.m.r. was thus used to characterize the isomeric structure and to quantify the isomer composition. It was found that the isomer ratios quantitatively correlate with electron affinity of bridged dianhydrides and is independent of the alcohol structure used. Furthermore, the ^{1}H n.m.r chemical shift of bridged diester-diacids was found to be a very sensitive probe of chemical nature of bridged groups and can be used as indices of the opening selectivity. © 1997 Elsevier Science Ltd.

(Keywords: poly(amic ester); open selectivity; n.m.r. chemical shift)

INTRODUCTION

The synthesis of poly(amic ester)s has been encouraged by their increased hydrolytic stability in solution, improved solubility, higher imidization temperature regime that offers a wider processing window for good adhesion[1–11]. Initial step for the synthesis of poly(amic ester)s involves the esterification of aromatic dianhydrides. Since the alcohol can attack either of the anhydride carbonyl groups, it results in the formation of several isomers of aromatic diester-diacids (*Figure 1*), and the obtained poly(amic ester)s are a copolymer containing several different repeat unit isomers whose isomerism was dependent on the isomerism of aromatic diester-diacids starting material[12]. The separation of the respective structural isomers of aromatic diester-diacids and preparation of the corresponding isomerically pure poly(amic ester)s have permitted the investigation of the effect of the isomerism of the repeat units on the curing behaviour of the polymer[9,10,13], which theoretical considerations have led to the predication that the percent imidization expected for pure *para-*, *meta-* and mixed *meta-/para-*additions of the poly(amic acid)s prepared from pyromellitic dianhydride (PMDA) are 100, 82 and 92%, respectively[14]. This effect is predicted to arise from the relative difficulty of bringing the amide functionality into the correct geometry to react with the –OH group of the acid, similar theoretical analysis for poly(amic acid)s with bridged dianhydrides had shown conformational barriers may also be high[15]. It has been found that these different repeat units of poly(amic ester)s have shown distinct differences in solubility[9,10].

We have undertaken the synthesis of the poly(amic ester), the existence of the isomerism of aromatic diester-diacids starting material promoted us to develop an analytical method for determining the opening selectivity of dianhydride groups towards alcohols. In this respect high resolution ^{1}H n.m.r. spectroscopy provides a more convenient method for rapid routine analysis.

In this paper we used the high resolution ^{1}H n.m.r. spectrometer to characterize the isomeric structure of aromatic diester-diacids and to investigate the ring opening selectivity of aromatic anhydride groups. Since the opening of anhydride groups can be affected by the chemical structure of dianhydrides, it was decided to determine its influence on the stereospecificity of anhydride group opening and on ^{1}H n.m.r. chemical shift of aromatic diester-diacids.

EXPERIMENTAL

Materials

Figure 2 illustrates the dianhydrides used in our work. The acronyms of these dianhydrides and their corresponding derived diester-diacids (prepared from methanol) are also listed. BPDA, DSDA, TDPA, HQDPA were prepared from 4-chlorophthalic anhydride in our laboratory[16–18], the others were available commercially. Dianhydrides were purified by sublimation or recrystallization prior to use. Alcohols used were distilled under nitrogen from CaH_2.

Measurements

High resolution ^{1}H n.m.r. spectra were recorded with a Varian Unity-400 spectrometry. The ^{1}H chemical shift were read directly from internal tetramethylsilane (TMS). All samples were dissolved in dimethylsulfoxide-d_6 (DMSO-d_6).

High performance liquid chromatography (h.p.l.c.) was performed on a GILSON h.p.l.c. system with a GILSON model 306 pump. A 250 × 4.6 mm i.d. reverse

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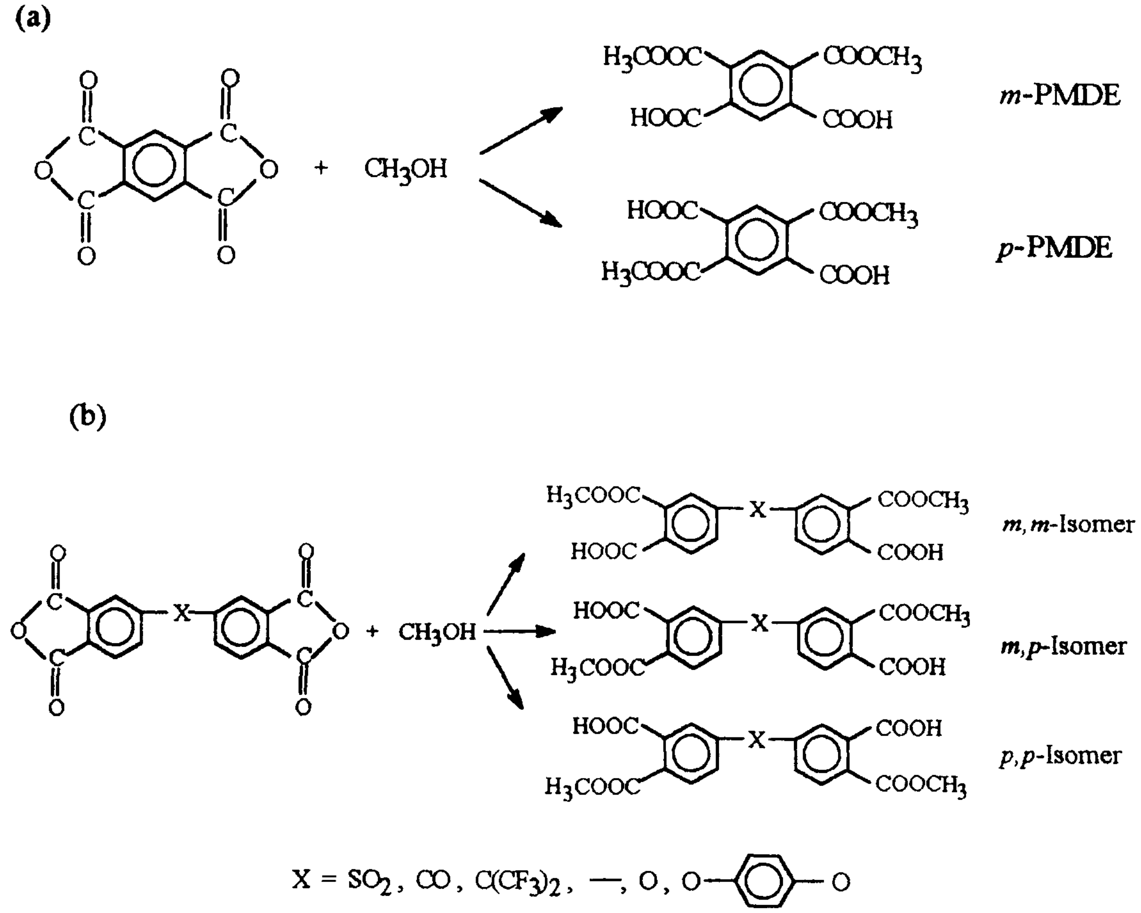

Figure 1 Synthesis of different aromatic diester-diacids isomers. (a) Two isomers of PMDE. (b) Three isomers of diester-diacids prepared from bridged dianhydrides

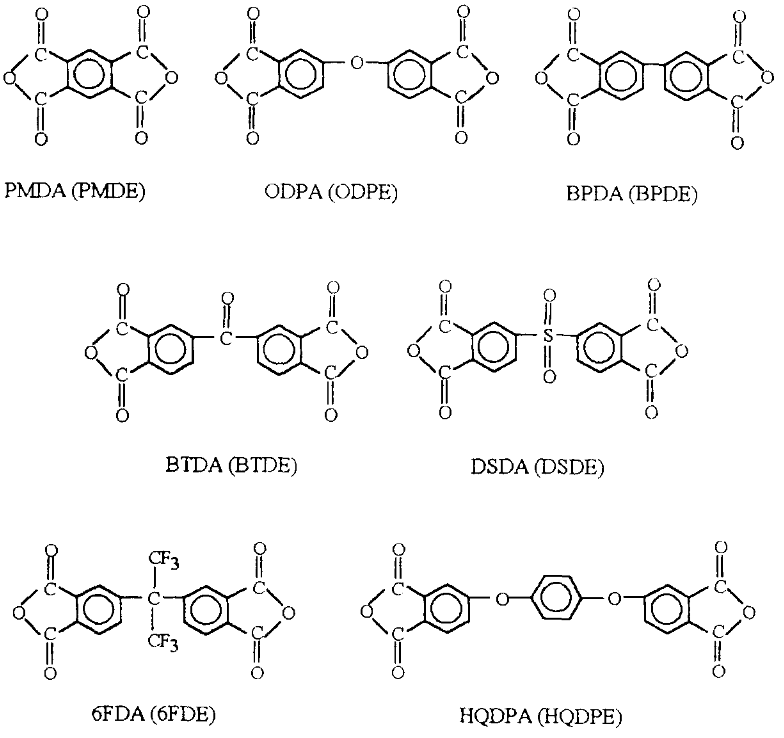
PMDA (PMDE)
ODPA (ODPE)
BPDA (BPDE)
BTDA (BTDE)
DSDA (DSDE)
6FDA (6FDE)
HQDPA (HQDPE)

Figure 2 The dianhydrides used in this study: PMDA = pyromellitic dianhydride; ODPA = 3,3′,4,4′-oxydiphthalic dianhydride; BPBA = 3,3′,4,4′-biphenyltetracarboxylic dianhydride; DSDA = 3,3′,4,4′-biphenylsulfone dianhydride; 6FDA = 6F dianhydride, 2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride; BTDA = 3,3′,4,4′-benzophenone-tetracarboxylic dianhydride; HQDPA = 1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride

Table 1 Melting point of aromatic diester-diacids

Diester-diacid	PMDE	BPDE	DSDE	ODPE	6FDE	BTDE	HQDPE
M.p. (°C)	242–243	170–172	180–182	168–170	75–78	154–156	271–272

phase column (Spherisorb ODS-2) was used. The wavelength of the detector was set to 254 nm. The solvent system was a 25/75 acetontrile/buffer solution and separation involved ionization suppression chromatography (i.s.)[19]. The ionization of carboxylic acid groups on aromatic diester-diacids was suppressed by using a pH = 3.0 NaH_2PO_4 buffer.

Aromatic diester-diacids were readily prepared by reaction of various alcohols with dianhydrides, and a detailed example of the main synthetic approach is shown below.

A 40 ml methanol solution containing 5.00 g of BTDA was refluxed under nitrogen and distilling off the methanol after a clear solution was obtained. Residual methanol was removed by adding 10 ml of toluene to the solution and continuing the distillation under vacuum. The product was obtained quantitatively as a white solid, m.p. 154–156°C.

RESULTS AND DISCUSSION

It was thought that esterification of dianhydrides has completed after all solids had gone into solutions, because the rate of reaction is controlled by the limit solubility of the dianhydrides in methanol rather than the rate of esterification of dianhydrides in solution. Water was excluded from the reaction in order to avoid the hydrolysis of the dianhydride to form the impurities[20,21]. The products prepared from bridged dianhydrides were viscous oils after distilling off methanol, and residual alcohol is extremely difficult to remove even though continuous distillation under reduced pressure was used[12,22–24]. The residual alcohol not only makes it hard to react in stoichiometric amounts, but is a contaminant in preparing high molecular weight poly(amic ester)s by peptide coupling reagent[12]. In our work the problem was resolved by adding a high boiling solvent such as benzene or toluene and consequently the residual alcohol can be removed by distilling under vacuum, or by recrystallization, and all aromatic diester-diacids afford a solid powder with a narrow melting temperature range (*Table 1*).

The nucleophilic attack by alcohol on dianhydrides can lead to the formation of several position isomers. In the case of PMDA, two isomers were expected, whereas in the case of bridged dianhydrides, three possible isomeric structures can be formed (*Figure 1*).

The ^1H n.m.r. study enabled structures to be attributed to these isomeric diester-diacids. The examination of the 7–9 ppm and 3–4 ppm regions, corresponding to aromatic protons and $-OCH_3$ protons respectively, furnished valuable data for the structural study of these compounds. There are two isomers for PMDE (*Figure 1a*), in the case of *p*-PMDE, which has a centre of symmetry, one line is expected from the protons of the PMDA skeleton (*Figure 3a*), whereas *m*-PMDE should present two different chemical shifts for aromatic protons, and this was observed in *Figure 3b*. The signals

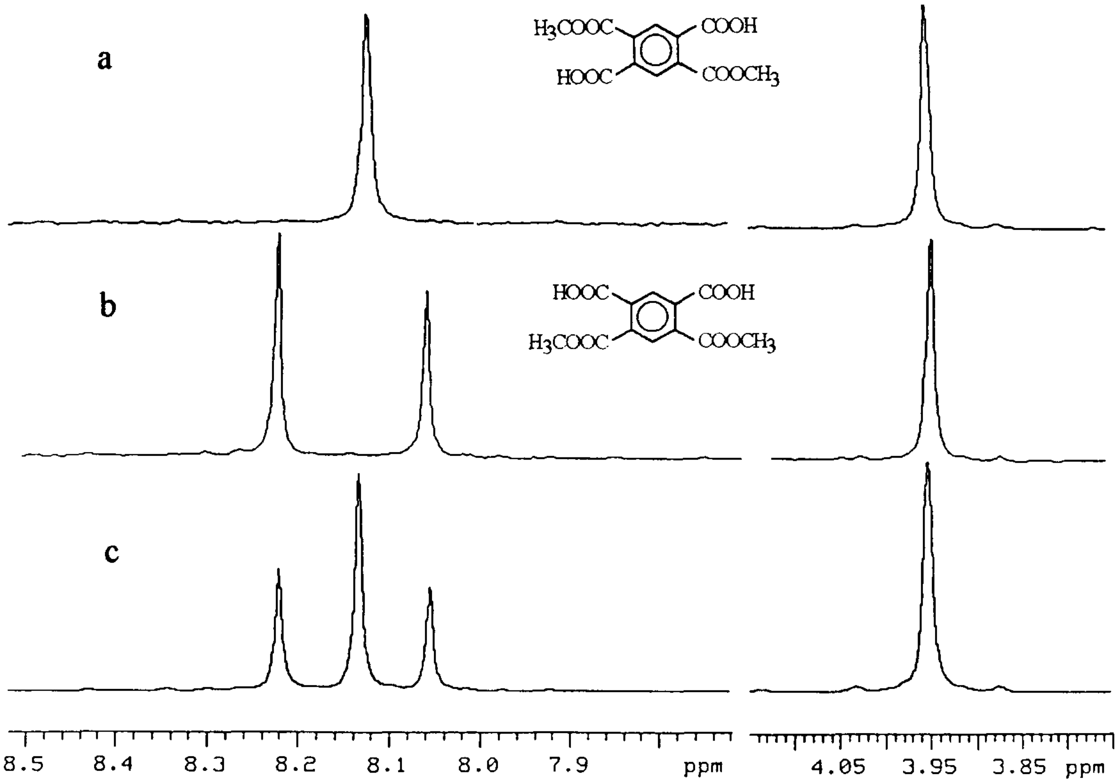

Figure 3 ^1H n.m.r. spectra of the two isomers and the mixtures of PMDE: (a) *p*-PMDE; (b) *m*-PMDE; (c) the mixtures

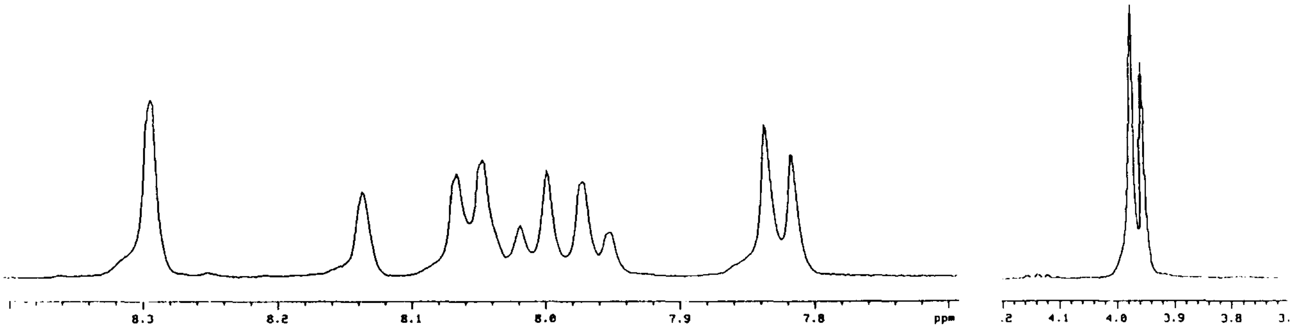

Figure 4 ^{1}H n.m.r. spectra of the three isomer mixtures of BTDE

of $-OCH_3$ protons in *m*-PMDA and *p*-PMDE are superimposed.

The separation of these two isomers is achieved by taking advantage of the much greater solubility of *m*-PMDE in organic solvents[13], and pure *m*-PMDE and *p*-PMDE is obtained after recrystallization. The amounts of *m*-PMDE and *p*-PMDE can be calculated from their respective signal intensities of the aromatic protons. It was found that PMDE consisted of 53% *m*-PMDE isomer and 47% *p*-PMDE isomer. The result agrees with the published data (0.54/0.46) by ^{1}H n.m.r. spectroscopy for analogous structural elements in the poly(amic acid) of PMDA and diamine[25], indicating that the *meta*-position is slightly preferred.

For aromatic diester-diacids prepared from bridged dianhydrides, three isomers were expected (*Figure 1b*). In the case of *m,m*-isomer and *p,p*-isomer, which has a centre of symmetry, one single peak and two double peaks in the aromatic region and one single peak in the $-OCH_3$ region should be expected, while *m,p*-isomer was expected to give two single peaks and four double peaks in the aromatic region and two single peaks for the $-OCH_3$ protons. The proton signals predicted for *m,p*-isomer would each be expected to superimpose with their counterparts in *m,m*-isomer and *p,p*-isomer due to their similar chemical environments. The ^{1}H n.m.r. spectra were observed as expected for all bridged aromatic diester-diacids, with a few exceptions that the signals were superimposed. One of these spectra was shown in *Figure 4*.

The presence of two single peaks and two double peaks only in the spectra, however, does not discount the possibility of all three isomers being present. Therefore, h.p.l.c. has been used to separate the isomer mixtures and three perfectly defined peaks confirmed the presence of the three isomers (*Figure 5a*).

The presence of the three isomers made it difficult to attribute the ^{1}H n.m.r. spectra of mixtures of diester-diacids due to overlap of proton signals. Attribution was facilitated, however, since fractionated crystallization in

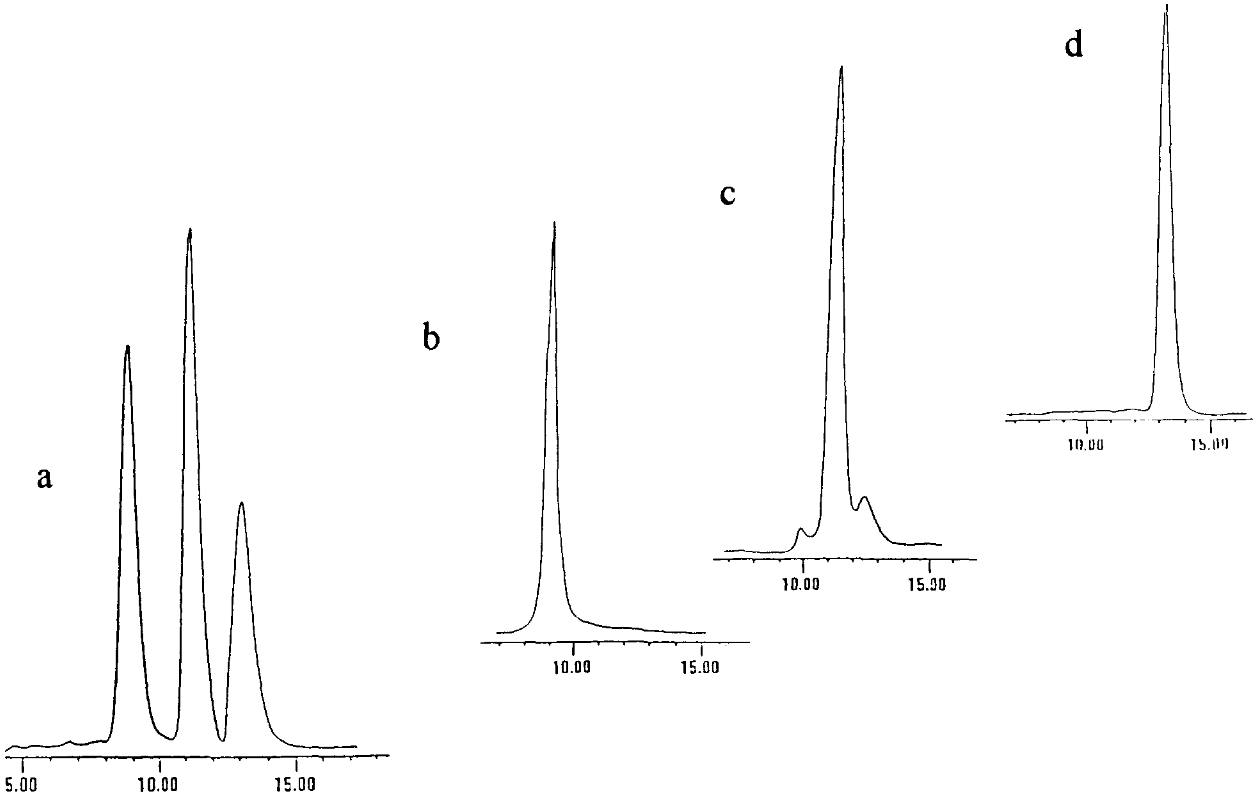

Figure 5 H.p.l.c. separation of the different isomers of BPDE: (a) the isomeric mixtures; (b) *m,m*-isomer; (c) *m,p*-isomer; (d) *p,p*-isomer

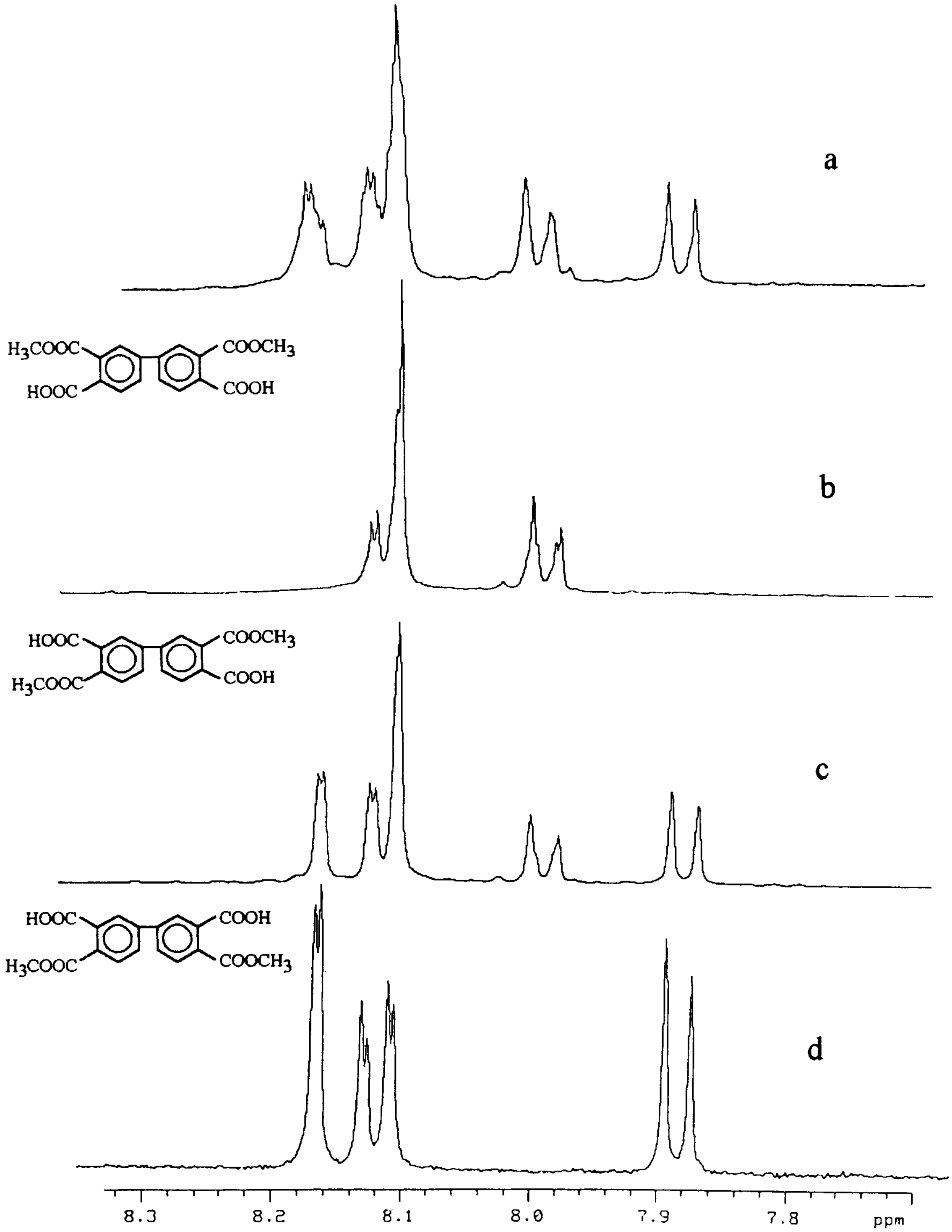

Figure 6 ^{1}H n.m.r. spectra of the three pure isomers and the mixtures of BPDE: (a) the isomeric mixtures; (b) *m,m*-isomer; (c) *m,p*-isomer; (d) *p,p*-isomer

some cases led to the isolation of three pure isomers of different series of diester-diacids[13]. The ^{1}H n.m.r. spectra of three pure isomers and their isomer mixtures of BPDE are shown in *Figure 6*. The h.p.l.c. study shows both *m,m*-isomer and *p,p*-isomer are in more than 99% purity, while *m,p*-isomer is in 88% purity (*Figure 5*). The lower field single peak ($\delta = 8.20$) in *Figure 6b, c* is attributed to *p,p*-isomer and one of the protons of *m,p*-isomer due to a proton situated *ortho* to a carboxylic acid group[12,25,26]. A slightly secondary splitting was observed in a single peak and a double peak due to long range coupling. By comparing the spectra of the mixtures to those of pure isomers, all the signals on the spectra could be attributed. The situation can be simplified by considering only one half of the isomer structure. Thus, two types of structural linkages were obtained with the $-COOCH_3$ group in the *meta-* or *para*-position to the bridged groups (*Figure 7*). The relative abundance of the two types of structural linkages can be calculated by their respective signal intensity. The ^{1}H n.m.r. chemical shifts and relative abundance of types I and II were summarized in *Table 2*.

The opening selectivity of anhydride groups depends on the dianhydride structure[29]. *Meta*-position attack is

Table 2 ^1H n.m.r. chemical shifts (ppm), EA (eV) and relative abundance of *meta*- and *para*-postions

		Relative abundance		Chemical shift							
Diester-diacids	EA[a]	*Para*	*Meta*	H_a[b]	H_b	H_c	H_d	H'_a	H'_b	H'_c	H'_d
DSDE	1.57	0.62	0.38	8.47	8.43	8.01	3.93	8.40	8.41	8.10	3.95
BTDE	1.55	0.57	0.43	8.29	8.11	7.93	3.94	8.17	8.09	8.03	3.92
6FDE	–	0.52	0.48	8.10	7.93	7.83	3.92	8.08	7.92	7.87	3.90
BPDE	1.38	0.43	0.57	8.17	8.12	7.87	3.91	8.11	8.12	7.99	3.90
ODPE	1.30	0.34	0.66	7.40	7.44	7.86	3.89	7.38	7.39	7.98	3.87
HQDPE	1.19	0.26	0.74	7.34	7.36	7.86	3.88	7.27	7.30	7.98	3.87

[a] From Pebalk *et al.*[28]

[b] For assignments see *Figure 7*

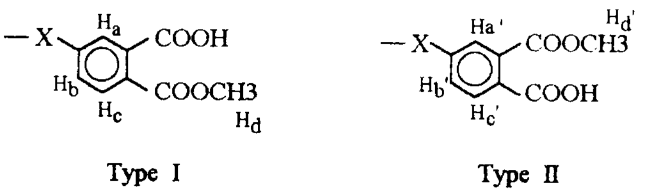

Figure 7 Two types of structural linkages of the bismethyl esters of bridged dianhydrides

slightly preferred in PMDA because the incoming methanol chooses between a carbonyl atom activated by –COOH group and a carbonyl atom activated by a –COOCH$_3$ group, and –COOH groups are slightly stronger electron-withdrawing groups. The preferred position of attack in bridged dianhydrides is determined by the chemical nature (donors or acceptors) of the bridged groups, since electron affinity (EA) is representative of electronic parameters that reflect donor and acceptor properties of the electron withdrawing ability of the bridged group. We examine the relationship between relative abundance of *para*- and *meta*-position isomers (types I and II) and EA. It can be seen that well-defined linear relationships exist between the percentage of *para*-position (P) and EA (*Figure 8*). The higher its EA values, corresponding to the stronger electron-withdrawing abilities, the higher is P. The relationship was thus used to estimate the EA values of dianhydride, 6FDA, which was not reported in the literature, as 1.48.

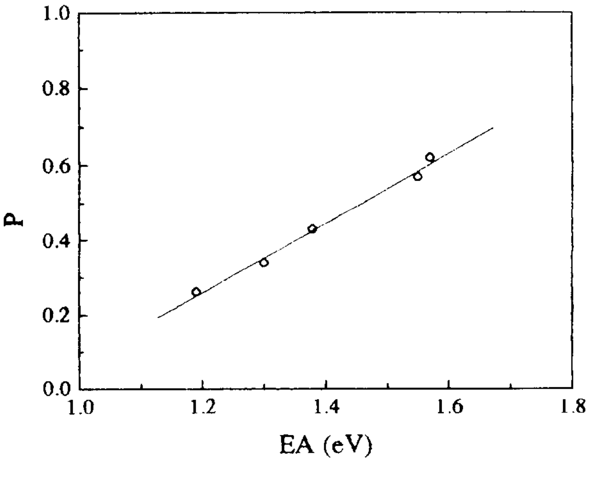

Figure 8 The percentage of *para*-position (P) plotted against electron affinity

The effect of bridged group on the ^1H n.m.r. chemical shifts of its diester-diacids is also examined (*Figure 9*). The ^1H n.m.r. chemical shifts are linear displaced downfield with increasing EA. For H_a (H_a^1) and H_b (H_b^1), *ortho* to the bridged groups, their chemical shifts show the same dependency of EA, and a lower slope was observed for protons H_c (H_c^1) *meta* to the bridged groups. The results show the ^1H n.m.r. chemical shift is a very sensitive probe of chemical nature of bridged groups. Since it is easier to observe than EA, it is interesting to estimate the ring opening selectivity of dianhydride by ^1H n.m.r. chemical shift of its diester-diacids.

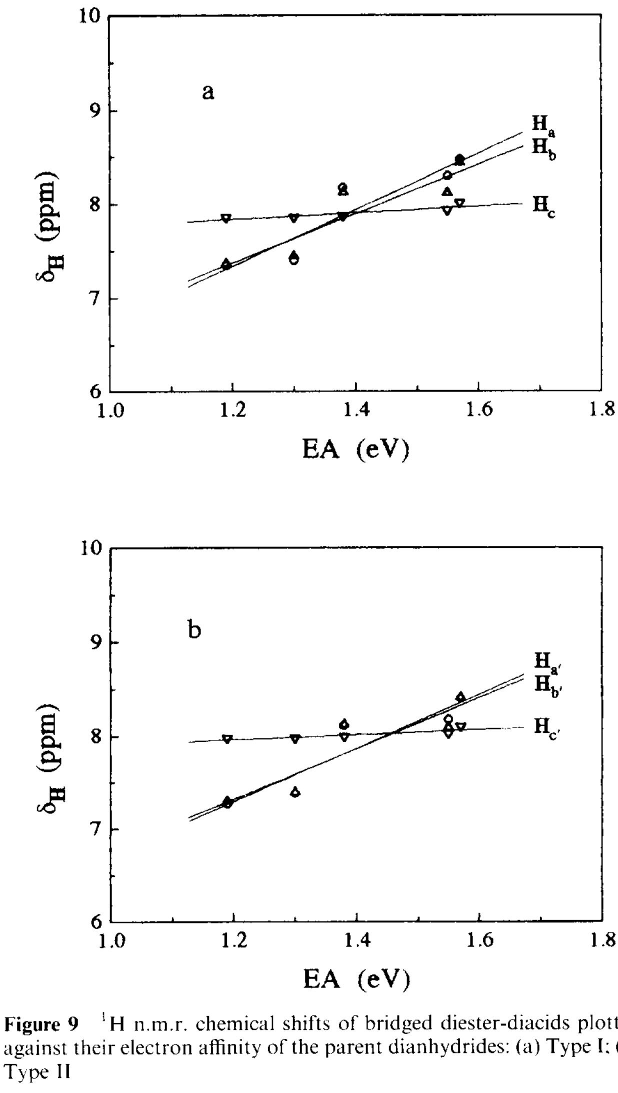

Figure 9 ^1H n.m.r. chemical shifts of bridged diester-diacids plotted against their electron affinity of the parent dianhydrides: (a) Type I; (b) Type II

The effect of different alcohols on the ring opening selectivity has been examined by ^1H n.m.r. A series of diester-diacids are prepared from BTDA and various alcohols (methanol, ethanol, isopropanol and *n*-butanol) and the percentage of *p-*/*m*-positions are calculated as 0.57/0.43, 0.54/0.46, 0.56/0.44 and 0.53/0.47, respectively. The results confirmed the ring opening selectivity of anhydride was independent of the alcohols used.

CONCLUSION

The ring selectivity of aromatic dianhydride towards methanol was studied by high resolution ^1H n.m.r. A well-defined linear relationship was obtained between the isomeric ratios and electron affinity where the *para*-position isomers increased as the electron-withdrawing ability of the bridge group increased. Additionally, the ring opening selectivity of anhydride was found to be independent of the alcohols used.

With the separation of well-defined isomerism of monomers, the isomeric poly(amic ester)s have been prepared from a series of bridged dianhydrides. Current work concentrates on a detailed investigation of the effect of the isomerism of the repeat units on the curve behaviour and solution properties.

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