Acetylene-terminated ether-ketone oligomers

F. Martínez Núñez and J. de Abajo*
Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva, 3,
28006 Madrid, Spain

and R. Mercier and B. Sillion
CEMOTA, BP 3, 63390 Vernaison, France
(Received 31 May 1991; revised 25 September 1991; accepted 7 October 1991)

A set of hydroxyl-terminated oligo(ether-ketones) based on isophthaloyl and oxyphenylene units were synthesized by conventional means involving Friedel–Crafts and Ullmann reactions. The pure dihydroxy intermediates were functionalized by end-capping with 3- and 4-ethynylbenzoylchloride. The synthetic route yielded oligomers of well defined composition, which could be readily confirmed by n.m.r. Solubility and thermal behaviour greatly depended on the ratio of *m*- to *p*-substituted phenylene rings present in the oligomers. All of the oligomers cured to insoluble, thermally stable materials after heating to 150–300°C and showed glass transition temperatures at ~250°C.

(Keywords: reactive oligomers; poly(ether-ketones); aromatic polymers; crosslinking)

INTRODUCTION

Fully aromatic polymers have been studied and fabricated worldwide as engineering thermoplastics and high performance materials[1,2]. A modern family of such polymers, which has received particular attention, is that of poly(ether-ketones). Poly(ether-ether-ketone) (PEEK), and in general those polymers composed only of phenylene nuclei joined by ether and ketone linkages, are among the thermoplastic polymers with the best balance of properties. Because of its regular structure, PEEK is a partially crystalline polymer, has a high melting point and outstanding chemical resistance. On the other hand it is insoluble in organic solvents, which is a disadvantage for some applications.

Alternatives to barely processable polymers are the reactive oligomers, which may be dissolved in organic solvents or may be melted at relatively low processing temperatures[3,4]. This approach has been used in this study, which involves the synthesis, characterization and crosslinking of novel ether-ketone oligomers of different chemical composition, functionalized by means of acetylene-bearing reactants.

Acetylene was chosen as the reactive end group because among the compounds commonly used, it offers a major advantage in terms of stability, curing temperature and thermal resistance of the final crosslinked material. Furthermore, convenient synthetic routes have recently been outlined for the preparation of acetylene-bearing reactants, so that the functionalization of oligomers by this approach is possible[5–9].

EXPERIMENTAL

Materials

All reagents, except for isophthaloyl chloride, were commercial reagents or technical grade and were used without further purification. Isophthaloyl chloride was prepared from isophthalic acid and excess thionyl chloride by the usual method, and recrystallized from n-hexane prior to use.

Anisole and the solvents were purified by conventional means and finally distilled prior to use.

4-Phenoxyanisole was prepared from 4-bromoanisole and phenol by an Ullmann reaction as described elsewhere[10].

Synthesis of oligomers and intermediates

1,3-Bis(4-hydroxybenzoyl)benzene. $AlCl_3$ (67.5 g, 0.506 mol) and dry methylene chloride (70 ml) were mixed in a three-necked round bottom flask. On the ice-cooled stirred dispersion were dropped isophthaloyl chloride (47.5 g, 0.234 mol) and anisole (52.3 g, 0.484 mol) dissolved in dry methylene chloride (100 ml). Then the ice bath was removed and the reaction was left to proceed at room temperature until the reactants were completely consumed. This took 4 h, and the end of the reaction was checked by thin layer chromatography. The mixture was poured on a large excess of ice–water and the solid that separated was filtered off. From the organic layer of the filtrate more solid was obtained by elimination of the solvent at reduced pressure. The product (73.5 g, 91%) was recrystallized from ethanol; m.p. 144°C.

The dimethoxy intermediate (68.6 g, 0.198 mol) was treated with acetic acid (500 ml) and hydrobromic acid (350 ml, 45%) at 120°C for 50 h. After cooling the mixture was poured on ice–water (2 l) and the precipitate that formed was filtered off, washed several times with water, and dried in a vacuum oven over P_2O_5 for 8 h. A white powder (62.2 g, 99%) was obtained. It was recrystallized from acetic acid:water (6:1); m.p. 216°C.

Elemental analysis for $C_{20}H_{14}O_4$. Calculated: C, 75.47%; H, 4.40%. Found: C, 75.38%; H, 4.54%.

I.r.: O–H, 3640–3200 cm^{-1}; C=O, 1620 cm^{-1}.

---

*To whom correspondence should be addressed

0032-3861/92/153286–06

^1H n.m.r.: aromatic protons between 8.10 ppm and 6.80 ppm [in dimethylsulphoxide (DMSO-d_6) with tetramethylsilane (TMS) as internal reference].

1,3-Bis(4'-hydroxy-4-phenoxybenzoyl)benzene (IP). 1,3-Bis(4'-methoxy-4-phenoxybenzoyl)benzene was synthesized by the procedure described above from isophthaloyl chloride and 4-phenoxyanisole. The product (84%) was recrystallized from ethanol; m.p. 159°C.

The dihydroxylated oligomer was prepared from the dimethoxy intermediate by the described method of hydrolysis with acetic acid and hydrobromic acid. The product (84%) was recrystallized from ethanol:water (2:1); m.p. 225°C.

Elemental analysis for $C_{32}H_{22}O_6$. Calculated: C, 76.48%; H, 4.41%. Found: C, 76.01%; H, 4.65%.

I.r.: O–H, 3600–3100 cm^{-1}; C=O, 1630 cm^{-1}.

^1H n.m.r.: aromatic protons between 8.20 ppm and 6.50 ppm, OH signal at 9.50 ppm (in DMSO-d_6 with TMS as internal reference).

1,3-Bis(3'-hydroxy-4-phenoxybenzoyl)benzene (IM): 1,3-Bis(4-hydroxybenzoyl)benzene (42.0 g, 0.132 mol) and ground KOH (14.2 g, 0.254 mol) were thoroughly mixed in a dry box and transferred to a 250 ml flask fitted with a mechanical stirrer, gas inlet, and outlet connected to a distillation cooler. The mixture was heated under N_2 to 180°C for 4 h, when the separation of water ceased. Residual water was eliminated under low pressure and then 3-bromoanisole (49.4 g, 0.264 mol) was added together with active copper (0.5 g, 7.9 mmol). The mixture was left to react for 8 h at 230°C and, once cooled, extracted with methylene chloride. Residual unreacted bisphenolate was taken off by shaking the solution with aqueous NaOH, and unreacted 3-bromoanisole was eliminated by vapour stream distillation. The solid product was washed with water several times and dried in a vacuum oven overnight. The crude product (31.3 g, 47%) was recrystallized from ethanol; m.p. 106°C.

The dihydroxylated oligomer was prepared from the dimethoxy intermediate by the usual method with refluxing acetic acid and hydrobromic acid. The oligomer was isolated by pouring the acidic solution on a large excess of ice–water. The product (98%) was recrystallized from ethanol:water; m.p. 196°C.

Elemental analysis for $C_{32}H_{22}O_6$. Calculated: C, 76.48%; H, 4.41%. Found: C, 76.18%; H, 4.48%.

I.r.: O–H, 3600–3100 cm^{-1}; C=O, 1640 cm^{-1}.

^1H n.m.r.: aromatic protons between 8.20 ppm and 6.50 ppm, OH signal at 9.75 ppm (in DMSO-d_6 with TMS as internal reference).

4-Ethynylbenzoylchloride (4-EBC). This reactant was prepared by a six-step synthetic route as follows: 4-bromobenzaldehyde (92.5 g, 0.500 mol) and a few drops of acetic acid were dissolved in methanol (200 ml). Under a gentle flow of argon, propylamine (34 g, 0.500 mol) was dropped on the solution and, after 2 h, dry Na_2SO_4 was added to trap the water from the reaction. The solid was filtered off and 4-bromobenzaldimine (113.0 g, ~100%) was obtained as a mobile liquid after evaporation of the solvent.

4-Bromobenzaldimine (105.0 g, 0.465 mol), 2-methyl-3-butin-2-ol (MBO, 42.9 g, 0.500 mol) and deoxygenated triethylamine (350 ml) were heated to 80°C under argon, and palladium-bis(triphenylphosphine)-dichloride (0.445 g, 0.63 mmol), triphenylphosphine (0.766 g, 0.92 mmol) and CuI (0.144 g, 0.76 mmol) were added to the stirred solution. After 4 h, the mixture was filtered and the solid (triethylaminebromohydrate) was washed with triethylamine on the filter. The solvent was distilled off under vacuum and the solid residue was dried in a vacuum oven. Dry 4-(3-methyl-3-ol)butin-*N*-propylbenzaldimine (106.0 g, ~100%) was isolated; m.p. 92°C (d.s.c.).

4-(3-Methyl-3-ol)butin-*N*-propylbenzaldimine (105.0 g, 0.458 mol) was heated with toluene (350 ml) to 100°C under argon and powdered NaOH (2.0 g) was added to the solution. After 5 h, charcoal was added to the reaction mixture, which was stirred at 80°C for 30 min and filtered on Celite. The filtrate was vacuum rotated and the residue was distilled on a small amount of hydroquinone. The fraction distilling at 55–57°C (0.04 mmHg) was collected and identified as 4-ethynyl-*N*-propylbenzaldimine (69%).

4-Ethynyl-*N*-propylbenzaldimine (51.0 g, 0.298 mol) was dropped at room temperature on an acidic aqueous solution containing HCl (0.314 mol). After 30 min the white precipitate formed during the reaction was filtered off, washed with water and dried in a vacuum oven over P_2O_5 for 24 h. Dry 4-ethynylbenzaldehyde (38.5 g, ~100%) was obtained; m.p. 97–98°C (lit. 88–90°C)[6].

4-Ethynylbenzoic acid was prepared by heating the aldehyde (17.0 g, 0.130 mol) and sodium perborate (19.5 g) in acetic acid (60 ml) at 80°C for 30 min. The precipitate was filtered off upon cooling, washed with water and dried in a vacuum oven to obtain the acid (17.0 g, 90%); m.p. 223–224°C.

To a dispersion of the acid (6.5 g, 0.045 mol) in methylene chloride (65 ml), PCl_5 (10.1 g, 0.048 mol) was added in stages over 5 h at 40°C. Once the reaction had finished, the clear mixture was vacuum rotated and the solid dry residue was collected and recrystallized from n-hexane. Pure 4-EBC (6.2 g, 85%) was isolated; m.p. 79–80°C (lit. 74.5–76°C[8]).

Elemental analysis for C_9H_5ClO. Calculated: C, 65.65%; H, 3.07%; Cl, 21.54%. Found: 65.63%; H, 3.19%; Cl, 21.35%.

I.r.: C–H, 3330 cm^{-1}; C=O, 1790 and 1750 cm^{-1}.

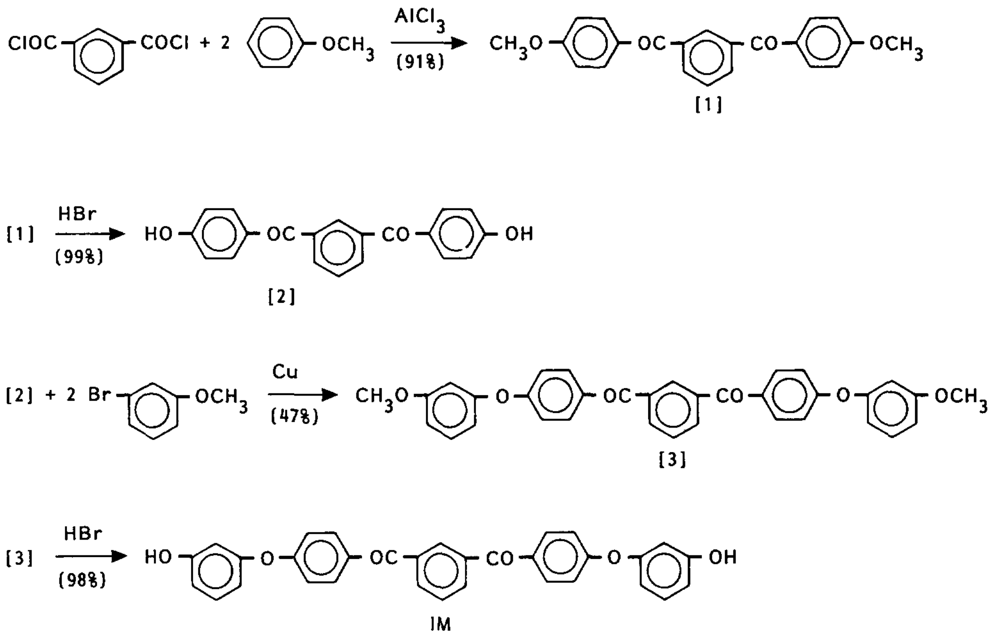
^1H n.m.r. aromatic system centred at 7.85 ppm, CH signal at 3.35 ppm (in $CDCl_3$ with TMS as internal reference).

3-Ethynylbenzoylchloride (3-EBC). The starting material was 3-ethynylbenzaldehyde, which was first synthesized from 3-bromobenzaldehyde by the method described elsewhere[6]. It was oxidized to 3-ethynylbenzoic acid (84%) with sodium perborate in acetic acid by the same method used for 4-ethynylbenzaldehyde; m.p. 174°C. The acid was made to react with PCl_5 in methylene chloride at 40°C for 30 min, then the solvent and side products were distilled off, and the acid chloride (3-EBC, 87%) was taken out at 53–55°C/0.1 mm Hg.

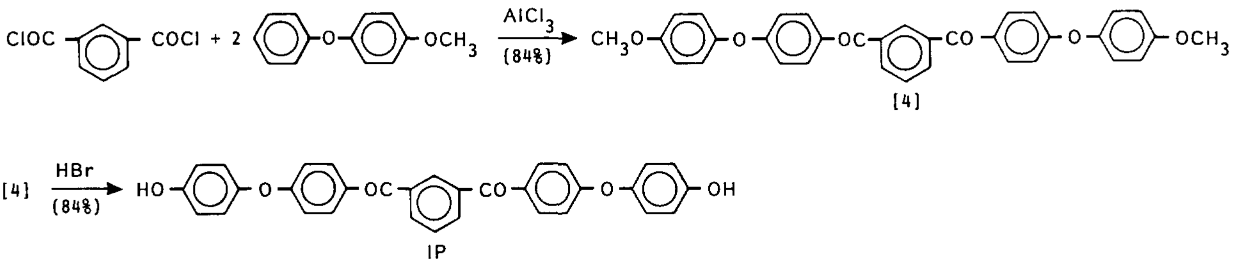
Elemental analysis for C_9H_5ClO. Calculated: C, 65.65%; H, 3.07%; Cl, 21.54%. Found: C, 65.40%; H, 3.11%; Cl, 21.50%.

I.r.: C–H, 3300 cm^{-1}; C=O, 1760 cm^{-1}.

^1H n.m.r. aromatic protons between 8.30 ppm and 7.30 ppm, CH signal at 3.20 ppm (in $CDCl_3$ with TMS as internal reference).



Scheme 1 Synthetic route for intermediate IM



Scheme 2 Synthetic route for intermediate IP

Synthesis of functionalized oligomers. As an example of the general procedure, the functionalization of oligomer IM with 3-EBC is described here. Oligomer IM (8.0 g, 16 mmol), triethylamine (3.6 g, 36 mmol) and dimethylaminopyridine (0.42 g, 3.5 mmol) were dissolved in dry tetrahydrofuran (80 ml). A solution of 3-EBC (5.6 g, 34 mmol) in tetrahydrofuran (80 ml) was slowly dropped onto the stirred reaction mixture over 3 h. After 2 h at room temperature, the solid (10.8 g, 89%) was filtered off, washed several times with water and once with methanol, and dried in a vacuum oven at room temperature over P_2O_5; m.p. 130°C.

Measurements

Elemental analyses were carried out by the Analyses Service of the Centro Nacional de Química Orgánica (Madrid). I.r. spectra were recorded on a Perkin-Elmer 457 spectrometer in KBr pellets. N.m.r. spectra were recorded in a XL-300 Varian spectrometer in $CDCl_3$ or DMSO with TMS as internal reference.

Melting points were determined visually using a Buchi apparatus, and occasionally by d.s.c.

D.s.c. curves were run in a Perkin-Elmer DSC-4 device joined to a data station 3600, using aluminium pans. The experiments were performed under N_2 at 10°C min^{-1}.

Thermogravimetric analyses were carried out with a Perkin-Elmer TQS-2 thermobalance, by the dynamic method under N_2 at 10°C min^{-1}.

Thermomechanical analyses were performed with a Perkin-Elmer TMS-2 device. Penetration and expansion modes were used, and the measurements were carried out under N_2 at 20°C min^{-1}. Samples were prepared by melting the reactive oligomers in small moulds and applying an appropriate cure schedule.

RESULTS AND DISCUSSION

The intermediates, hydroxy-terminated oligomers, were prepared through the synthetic pathways shown in *Schemes 1* and *2*. Preliminary attempts to synthesize a series including isophthaloyl and terephthaloyl moieties led to only isophthaloyl derivatives being used for this study due to the very high melting points and very poor solubility of terephthaloyl oligomers.

The intermediates IM and IP could be prepared in reasonably good yields by the traditional methods involving Friedel–Crafts and Ullmann reactions. They were purified by successive recrystallizations, and identified by elemental analyses, and i.r. and n.m.r. spectroscopies.

3-EBC and 4-EBC were used as reactants for the end-capping of the hydroxy-terminated oligomers in order to attain the final oligomers with acetylene reactive groups. 3-EBC could be synthesized by the method previously described[6], but for the preparation of 4-EBC an alternative synthetic route was used (*Scheme 3*). This

Table 1 Acetylene-terminated ether-ketone oligomers

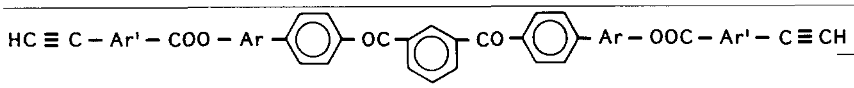
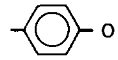
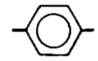
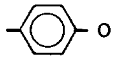
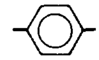
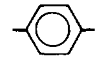
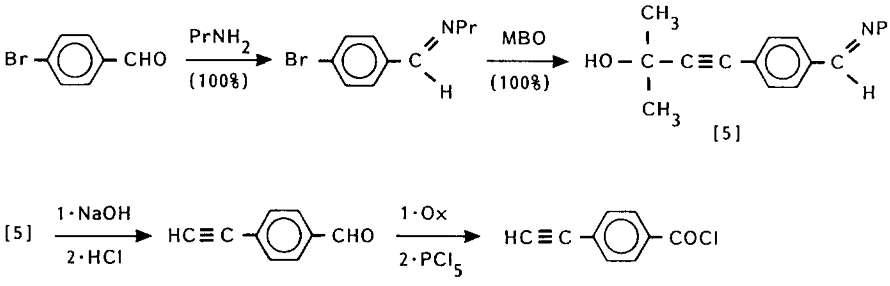
				Elemental analysis			
				C (%)		H (%)	
Reactive oligomer	Ar	Ar′	Yield (%)	Calc.	Found	Calc.	Found
OPP			94	79.15	78.63	3.99	4.01
OPM			91	79.15	78.80	3.99	4.11
OMP			80	79.15	78.04	3.99	4.06
OMM			89	79.15	78.79	3.99	4.00
OBP	-		75	79.44	78.19	3.87	3.96
OBM	–		94	79.44	78.35	3.87	4.13

Table 2 I.r. frequencies for absorption bands and n.m.r. chemical shifts of acetylene-terminated oligo(ether-ketones)

	I.r.				N.m.r.[a]				
					^{1}H	^{13}C			
	C≡C	C–H	C=O (ketone)	C=O (ester)	≡C–H	–C≡	≡C–H	–C=O (ketone)	–C=O (ester)
OPP	2095	3270	1640	1735	4.36	83.54	82.17	193.28	163.54
OPM	–	3290	1640	1735	4.34	81.73	81.97	193.50	163.58
OMP	2100	3270	1650	1730	4.50	83.74	82.21	193.35	163.33
OMM	–	3280	1650	1735	4.34	81.88	81.99	193.54	163.37
OBP	2100	3270	1655	1730	4.36	83.87	82.21	193.65	163.21
OBM	2100	3280	1645	1725	4.35	81.60	81.84	193.68	163.07

[a] Measured at 60°C



Scheme 3 Synthesis of 4-EBC

method involved the protection of the aldehyde group in the first step, but this additional protection–deprotection process was well justified by the high reaction yields (virtually quantitative) and by the use of MBO, which is much cheaper than trimethylsilylacetylene.

The esterification of the intermediates IM and IP with the two reactants having acetylene groups led to four functionalized oligomers through a Schotten–Bauman acylation reaction at room temperature. Furthermore, the intermediate **2** was also taken as a 'short' dihydroxy oligomer and esterified in the same way with 4-EBC and 3-EBC, so that six reactive oligomers were available. The reaction yields and elemental analyses are shown in *Table 1*.

I.r. frequencies for most significant absorption bands and n.m.r. chemical shifts of the acetylenic hydrogen and carbons are listed in *Table 2*. I.r. spectroscopy could readily distinguish the strong absorptions due to carbonyl stretching vibrations of aromatic ketones and esters at 1650 and 1735 cm^{-1}, respectively; the C–O–C stretching of esters and aromatic ethers in the region 1160–1280 cm^{-1}; the C–H stretching vibration of the ethynyl group at 3280 cm^{-1}; the bands ascribed to C=C stretching of aromatic bonds in the region 1445–1600 cm^{-1}; and bands attributed to the out-of-plane bending of the benzene C–H bonds in the region 650–800 cm^{-1}. However, the band of C≡C stretching that should appear at 2100 cm^{-1} was only detectable in

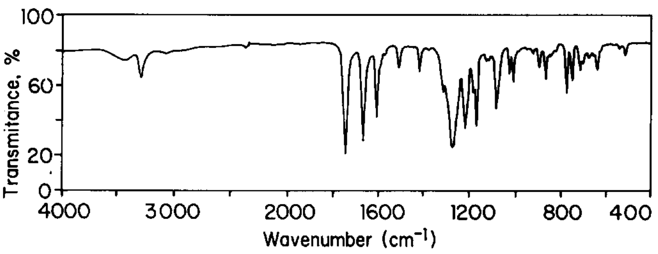


Figure 1 I.r. spectrum of oligomer OBP

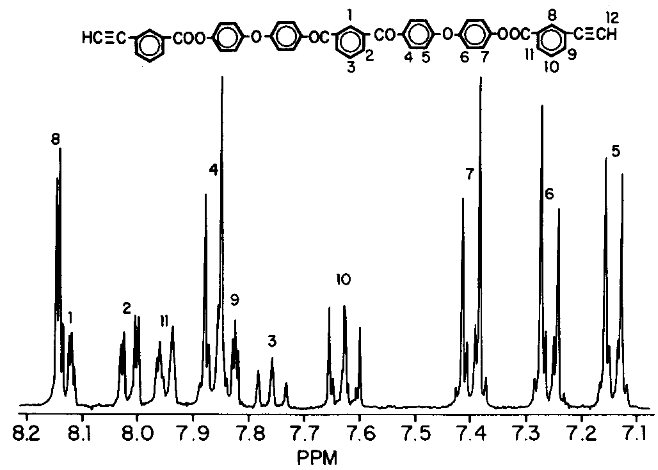


Figure 2 300 MHz ^{1}H n.m.r. spectrum (aromatic region) of oligomer OPM

most cases as a very slight signal and virtually invisible for oligomers OPM and OMM. The i.r. spectrum of oligomer OBP is given in *Figure 1*.

As to the n.m.r. analyses, the data collected in *Table 2* cover all the oligomers in spite of the very poor solubility of some of them. In the case of oligomers OPP and OBP, only 1–2 mg could be dissolved in DMSO-d_6 and transferred to the n.m.r. probes. On the other hand, the accumulation of 128 transients was sufficient to produce the spectra with a reasonable signal to noise ratio, even at such a low concentration. The ^{1}H n.m.r. spectrum of oligomer OPM is shown in *Figure 2*, and the assignments for the signals are given. The complicated pattern between 6 ppm and 8 ppm could be resolved, as the overlapping of some aromatic protons did not greatly disturb the assignments of all the peaks. On the other hand, the integral of this region fitted with the number of aromatic protons relative to the area of the two acetylenic protons that appeared at ~4 ppm. It is worth noting that special conditions had to be set to obtain accurate ^{1}H n.m.r. spectra in most cases. For instance, long acquisition times (10 s) between pulses had to be employed in order to obtain correct signals for all the protons. In particular, protons such as 1 and 12 (*Figure 2*), with no neighbouring hydrogen, did not relax fast enough and did not give correct peak areas unless long acquisition times were used.

Figure 3 shows the ^{13}C n.m.r. spectrum of oligomer OPM. In this case, as with the other members of the series, the assignment of the signals could be made without difficulty. This confirmed unambiguously the chemical nature of the oligomers. Acceptable spectra for the less soluble materials were obtained after 50000 transients. Furthermore, the absence of other non-assignable peaks, here and in the ^{1}H n.m.r. spectra, should be taken as a proof of the degree of purity achieved in the oligomer syntheses.

Suitable crosslinkable materials for technical applications must either be soluble in available solvents or melt without decomposition at a temperature below the curing reaction. For the present oligomers, common solvents were not enough and only very polar solvents such as DMSO or dimethylacetamide (DMA) were capable of dissolving them. Oligomers OPP and OBP were soluble in DMSO and DMA at very low concentrations. Therefore, the method used should be thermal curing in the melt.

The curing of acetylene-terminated oligomers has been investigated in many instances[5,11–14]. The calorimetric method (d.s.c.) is by far the main method used here to study the thermal behaviour and the crosslinking of these materials.

The melting temperatures of the oligomers are listed in *Table 3*. They lie in the range 130–215°C (melting endotherm onset). The curing temperature of previously reported acetylene compounds is in the range 140–200°C[15], so that only those oligomers with the lowest m.p. can be envisaged as favourable to be studied as curing materials. The d.s.c. curve of oligomer OMM (m.p. 130°C) is shown in *Figure 4*. It shows a 'processing window' (temperature interval between melting and curing) of ~40°C, which enables it to be applied in the melt and subsequently to be cured from 185°C. It is noteworthy that OMM shows the greatest ratio (5/2) of *m*- to *p*-phenylene rings of the

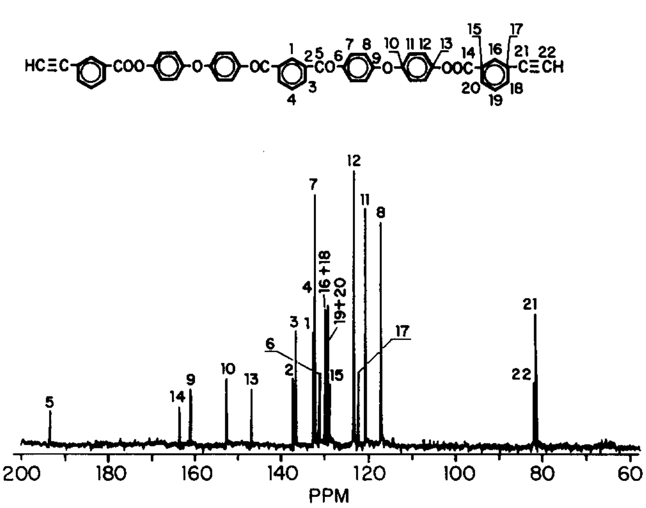


Figure 3 ^{13}C n.m.r. spectrum of oligomer OPM

Table 3 Thermal behaviour of oligo(ether-ketones)

Oligomer	T_m[a] (°C)	T_c[b] (°C)	T_g[c] (°C)	T_d[d] (°C)	R_{600}[e] (%)
OPP	215	241	–	460	69
OPM	186	264	250	430	70
OMP	167	252	235	440	73
OMM	130	268	210	415	68
OBP	–	251	–	400	65
OBM	210	252	230	375	65

[a] Oligomer m.p. (endothermal onset by d.s.c.)
[b] Exotherm peak temperature
[c] Glass transition temperature of the cured material
[d] Onset temperature of the thermal decomposition initiation
[e] Char residue at 600°C by dynamic t.g.a. (N_2, 10°C min^{-1})

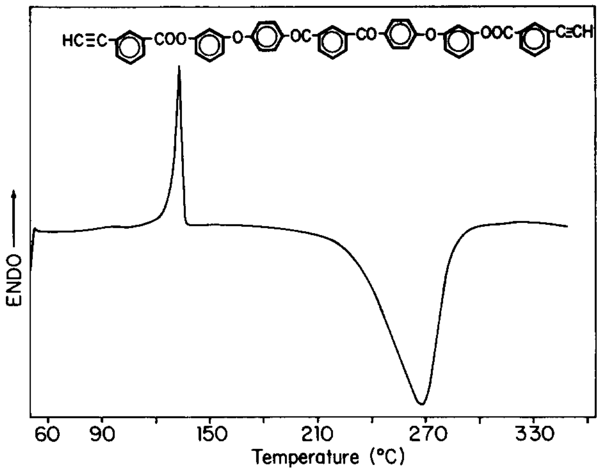


Figure 4 D.s.c. trace of oligomer OMM (N_2, 10°C min^{-1})

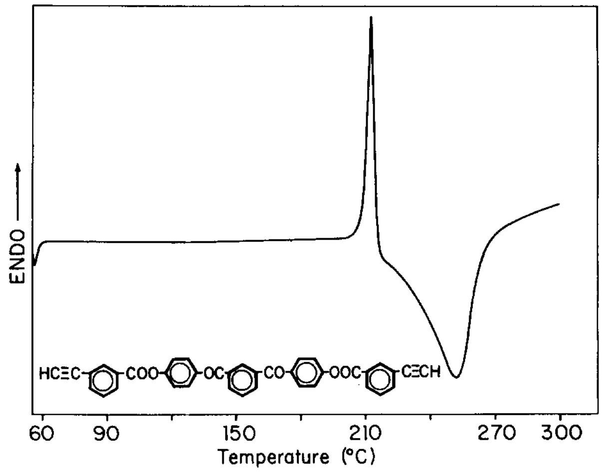


Figure 5 D.s.c. trace of oligomer OBM (N_2, 10°C min^{-1})

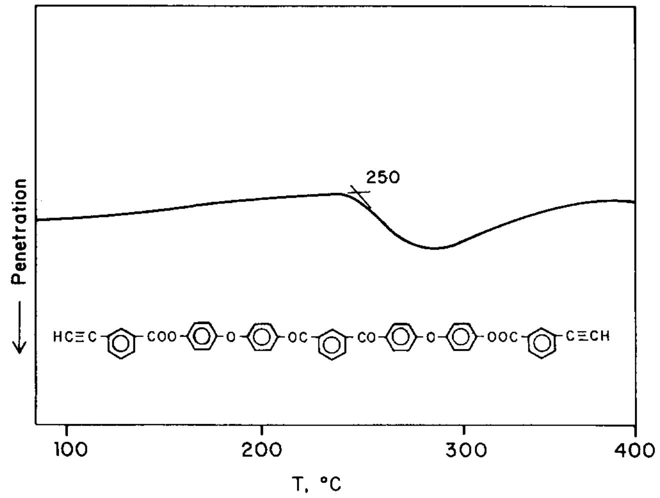


Figure 6 T.m.a. curve of oligomer OPM (N_2, 20°C min^{-1})

series. The other oligomers showed narrower processing windows and hardly showed, or did not show, a melt region in the d.s.c. curve between the melting endotherm and the curing exotherm. The d.s.c. trace of oligomer OBP is shown in *Figure 5*, where it can be seen that the crosslinking reaction exotherm greatly overlapped the melting endotherm. This means that the curing started before the melting process was completed. The consequence of such behaviour should be an imperfect material that only partially cures[16].

With the aim of exploring the properties of the crosslinked materials, the oligomers were cured by heating in air at 150°C/1 h, 250°C/1 h and 300°C/30 min. After this treatment, insoluble materials were obtained.

The glass transition temperatures (T_gs) of the polymer networks were investigated by d.s.c. and thermomechanical analysis (t.m.a.). No inflection of the d.s.c. curves assignable to the T_g could be detected in any case up to 350°C, even carrying out the experiments with high heating rates (40°C min^{-1}).

For highly crosslinked materials, with a dense network, t.m.a. is sometimes appropriate for determining thermal transitions. In fact, inflections that should be ascribed to T_gs could be detected in the t.m.a. measurements. The T_g data shown in *Table 3* indicate the comparatively high glass transitions achieved for these materials. The t.m.a. trace of OPM is shown in *Figure 6*. T_gs determined by this method lie between 210°C and 250°C (initial inflection onset). Linear aromatic *p*-oriented poly(ether-ketones), for instance, have a T_g of ~100°C lower than the cured oligo(ether-ketones)[2,17].

The thermal stability was investigated by programmed thermogravimetric analysis. All the materials were stable up to 400°C, with initial decomposition temperatures of ~440°C. The weight residue at 600°C in N_2 was >75% in most cases.

ACKNOWLEDGEMENT

Financial support provided by the CICYT (MAT88-0579-C02-01) is gratefully acknowledged.

REFERENCES

1 Critchley, J. P., Knight, G. J. and Wright, W. W. in 'Heat Resistant Polymers. Technologically Useful Materials'. Plenum, New York, 1983, p. 173
2 Rigby, R. B. in 'Engineering Thermoplastics. Properties and Applications' (Ed. J. M. Margolis), Dekker, New York, 1985
3 Reinhardt, B. A., Longhran, G. A., Arnold, F. E. and Soloski, E. J. in 'New Monomers and Polymers' (Eds B. M. Culbertson and C. N. Pittman), Plenum, New York, 1984, p. 29
4 Wallace, J. S., Arnold, F. E. and Feld, W. A. in 'Reactive Oligomers' (Eds F. W. Harris and H. I. Spinelli), American Chemical Society, Washington DC, 1985, p. 17
5 Kovar, R. F., Ehlers, G. F. L. and Arnold, F. E. *J. Polym. Sci., Polym. Chem. Edn* 1977, **15**, 1081
6 Austin, W. B., Bilow, N., Kelleghan, W. J. and Lau, K. S. J. *J. Org. Chem.* 1981, **46**, 2280
7 Harris, F. W., Pamidimukkala, A., Gupta, R., Das, S., Wu, T. and Mock, G. *J. Macromol. Sci. Chem* 1984, **A21**, 1117
8 Havens, S. J. and Hergenrother, P. M. *J. Polym. Sci., Polym. Chem. Edn* 1984, **22**, 3011
9 Delfort, B., Lucotte, G. and Cornier, L. *J. Polym. Sci., Polym. Chem. Edn* 1990, **28**, 2451
10 Walker, J. *J. Chem. Soc.* 1942, 347
11 Sefcik, M. D., Stejskal, E. O., McKay, R. A. and Sheefer, J. *Macromolecules* 1979, **12**, 423
12 Pickard, J. M., Jones, E. G. and Goldfard, I. J. *Macromolecules* 1979, **12**, 895
13 Hergenrother, P. M. *J. Macromol. Sci. Rev. Macromol. Chem.* 1980, **C19**, 14
14 Hergenrother, P. M. *Macromolecules* 1981, **14**, 891
15 Sillion, B. in 'Comprehensive Polymer Science' (Eds G. Allen and J. C. Bevington), Vol. 5, Pergamon, Oxford, 1989, p. 499
16 Stenzenberger, H. D. *Appl. Polym. Symp.* 1973, **22**, 77
17 Veda, M. and Sato, M. *Macromolecules* 1987, **20**, 2675