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New High-T_g, Heat-Resistant, Cross-Linked Polymers. 2. Synthesis and Characterization of Polymers from Di-*p*-ethynyl-Substituted Benzyl Phenyl Ether Monomers

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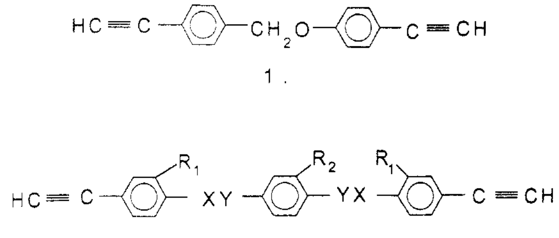
ABSTRACT: Six different neat di-*p*-ethynylbenzyl phenyl ether (EBEs) monomers were thermally polymerized. The progress and nature of the polymerization reaction were studied by FTIR, Raman, and DSC. The monomers had melting points between 94 and 197 °C. FTIR, Raman, and DSC showed that the monomers polymerized to high conversion after heating to 290 °C at 15 °C/min (no remaining acetylenic groups). The monomer DSC thermograms showed two intense exotherms. The first was correlated with the thermal polymerization of the acetylenic groups to form a polyene structure with unusually high enthalpies of polymerization, between 106 and 178 kJ/mol. The second DSC exotherm enthalpies varied between 31 and 64 kJ/mol and are due to further coupling of the polyene chains. The cross-linked resins exhibited an initial decomposition temperature in nitrogen between 389 and 410 °C; they had a very high anaerobic char yield (61–71% at 800 °C). The benzyl phenyl ether link was found to be thermally and thermooxidatively stable in the cured polymers. This was attributed to their high cross-link density. Well-consolidated, void-free films were obtained when the EBEs melt-polymerized. 4-Ethynyl-1-[(4-ethynylphenyl)methoxy]benzene (**1**) and 2,5-bis[(4-ethynylphenyl)methoxy]toluene (**4**) had wide "processing windows" of 55 and 40 °C, respectively, at a heating rate of 15 °C/min (DSC). The polymers of **4** and 1,4-bis[(4-ethynylphenyl)methoxy]-2-chlorobenzene (**5**) had T_g's of 364 and 330 °C, and their linear thermal expansions were 1.2 and 1% from room temperature to their T_g's. The cross-linked resins were amorphous. Their densities varied from 1.18 to 1.32 g/cm^3.

Introduction

Acetylene-terminated monomers can be cured thermally under moderate conditions without giving off volatiles. The polymers' high-temperature properties and moisture insensitivity have made them a promising material for high-temperature thermosetting systems. Oligomers and polymers containing acetylenic groups have excellent shelf lives and, when cured, provide resins with solvent resistance and a favorable combination of physical and mechanical properties. The cured resins are useful as functional (films and coatings) and structural resins (adhesives and composite matrices).[1] The ethynyl group has been used as a cure functionality in many different polymer classes including aromatic polyesters,[2] polyimides,[3,4] ether ketone sulfones,[5,6] phenylquinoxalines,[7] phenyl as triazines,[8] Schiff bases,[9] poly(perfluoroalkylene ether benzoxazoles),[10] poly(phenylquinoxalines),[11] and polyphenylenes.[12]

Many mechanisms have been proposed for the thermal polymerization of ethynyl-terminated monomers or oligomers. Model compound studies led to the proposal of biradical mechanisms forming linear or cyclic conjugated linkages.[13,14] It has also been speculated that a possible cure reaction is cyclotrimerization.[15] Other mechanisms proposed diyne structures due to Glaser coupling[11] and Friedel–Crafts alkenylation of the polymer backbone.[16]

One objective of this research was to study the polymerization mechanism. A second objective was to study the polymerization and the thermal stability of new polymers from di-*p*-ethynylbenzyl phenyl ethers (EBEs)[17] synthesized in our laboratory. The EBEs polymerized at moderately elevated temperatures in a short time to yield highly cross-linked, heat-resistant polymers, suitable as matrix resins for high-temperature composites. A requirement on the use of the EBEs was that these monomers should have a "processing window" between their melting point and the initiation of polymerization. EBEs are expected to posses improved flexibility and adhesion in the cured state while maintaining ease of processing and high thermal stability.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SAMPLE	X	Y	R₁	R₂
2	O	CH_2	H	H
3	O	CH_2	Cl	H
4	CH_2	O	H	CH_3
5	CH_2	O	H	Cl
6	CH_2	O	H	H

Figure 1. Chemical structures of di-*p*-ethynyl benzyl phenyl ether monomers, 1–6.

Experimental Section

Materials. The monomer syntheses and their properties were reported in the previous paper.[17] The monomer structures (1–6) are given in Figure 1.

Polymerization. (1) For the FTIR and Raman studies monomer **2** was partly polymerized between two glass slides (absence of air) after heating to 290 °C at 15 °C/min; it was also completely polymerized and postcured (between

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Table 1. DSC Data for Di-*p*-ethynyl-Substituted Benzyl Phenyl Ether Monomers, 1–6

		1st exotherm					2nd exotherm				
monomer	T_{melting} (°C)	T_i^a (°C)	$T_{\max}^b$ (°C)	T_f^c (°C)	ΔH_{pol} (kJ/mol)	ΔH_{pol} (J/g)	T'_i (°C)	$T'_{\max}$ (°C)	T'_f (°C)	ΔH_{pol} (kJ/mol)	ΔH_{pol} (J/g)
1	98	152	234	293	165	845	309	387	417	39	168
2	156	177	250	295	178	526	301	355	401	61	181
3	138	152	229	276	132	324	285	332	351	51	125
4	94	133	241	267	174	497	286	328	371	42	118
5	125	157	236	269	159	426	271	304	324	64	172
6	197	202	243	276	106	313	288	340	388	31	93

[a] Initiation temperature for polymerization. [b] Temperature of maximum polymerization rate. [c] Completion temperature for polymerization.

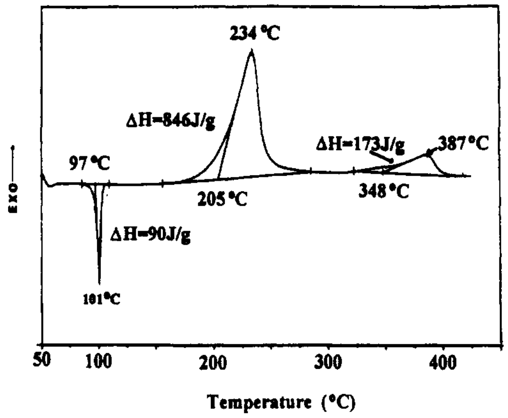

Figure 2. DSC of 1 at 15 °C/min in N_2.

two glass slides) by heating to 290 °C at 10 °C/min and held for 3 h at 290 °C. (2) For the TGA studies all monomers, **1–6**, were polymerized in air by heating them at 220 °C for 30 min and then at 250 °C for 1.5 h. They were postcured at 280 °C for 1.5 h. The resulting cross-linked resins of **1–6** are referred to as **1p–6p**, respectively, throughout the text.

Analytical Methods. Infrared spectra (FTIR) were recorded on a Bio-Rad Digilab FTS-60 spectrometer utilizing KBr pellets. Raman spectra were obtained on a DILOR XY Raman spectrometer with CCD detector and laser power 5.85 mW. X-ray scans were recorded using a Philips APD 3520 automatic diffractometer. Nickel-filtered Cu Kα radiation was used. Scans were run from 1° to 40° with a goniometer speed of 2°/min. A Carl Zeiss optical polarizing microscope equipped with a Mettler FP-82 hot stage and a Mettler FP 80 central processor was used to observe the thermal transitions. DSC scans were performed on a DuPont 2000 thermal analyzer with a heating rate of 15 °C/min in nitrogen at a flow rate of 50 mL/min. TGA measurements were performed on a DuPont 2000 analyzer with a heating rate of 15 °C/min and a gas flow rate of 50 mL/min. The TMA experiments were recorded on a DuPont 943 TMA using a 0.5-g expansion probe at 10 °C/min in static air. The densities of the polymers were measured using a density gradient column containing potassium bromide in water. Twenty-mil-thick pellets of the monomers were made by compression molding and polymerized using a hot stage.

Results and Discussion

The chemical structures of the *p*-ethynylbenzyl phenyl ethers (EBEs) **1–6**[17] synthesized in our laboratory are shown in Figure 1.

DSC Characterization. The curing behavior of **1–6** was examined by DSC (Table 1). A DSC thermogram representative of these monomers is shown in Figure 2. From Table 1 it can be seen that the monomers had melting points from 94 to 197 °C. Using hot-stage cross-polarized microscopy it was found that their clearing points and melting points were identical. All the monomers polymerized in the liquid state. For **1** and **4** there is a processing window of 55 and 40 °C, respectively, at a heating rate of 15 °C/min (DSC). This is an attractive feature[18] as most ethynyl-terminated monomers or oligomers[15] and commercial products such as Thermid 600 do not flow well at temperatures where the cure process begins. Thus, this wide processing window enables these polymer precursors to flow at low temperatures and cross-link at somewhat higher temperatures. The range of initiation of polymerization was 133–202 °C, depending on the specific EBE, and the range for termination was 267–295 °C (DSC thermograms). Upon cooling and reheating to 420 °C, there was no further reaction (no exotherm). The DSC thermograms of all monomers showed two exotherms (Figure 2). Their polymerization enthalpies varied from 106 to 178 kJ/mol for the first and from 31 to 64 kJ/mol for the second. Although many papers and patents over the last 15 years have discussed the reactions of ethynyl-terminated monomers or oligomers, none has reported a two-stage polymerization. Recently, Stevenson et al.[19] reported a very small second exotherm in the polymerization of bis[4-(3-ethynylphenoxy)phenyl] sulfone.

It was important to know whether the two stages were due to two different chemical reactions or a delayed reaction of any remaining ethynyl groups. The polymerization was followed by IR, Raman, and DSC. DSC was used to estimate the stage of polymerization or postcuring. Different heating rates and/or isothermal conditions were applied to separate the first exotherm from the second. Finally, heating monomer **2** to 290 °C between two glass plates (absence of air) at 15 °C/min on the hot stage yielded a resin which has only the second exotherm (Figure 3b). Heating monomer **2** to 290 °C and holding for 3 h in the absence of air yielded a resin with no exotherm at all (Figure 3c).

FTIR and Raman Studies. The FTIR spectra of monomer **2**, after heating to 290 °C in the absence of air at a heating rate of 15 °C/min in the hot stage, and after 3 h at 290 °C are shown in Figure 4. Figure 5 shows the Raman spectra of the same samples. The data show that the ethynyl groups had completely reacted by the time the system reached 290 °C. The absorption bands at 3273, 2100, and 627 cm^{-1} (Figure 4a) due to the C(sp)–H stretch, C(sp)–C(sp) stretch, and C(sp)–H bending vibrations of the acetylenic group completely disappeared after heating to 290 °C (Figure 4b). This was also confirmed by the Raman spectra (Figure 5). The C(sp)–C(sp) stretch at the 2103-cm^{-1} band disappeared completely after the initial heating. The evidence points to the generation of a polyene structure; the weak band at 3029 cm^{-1} (olefinic and aromatic C–H stretch; Figure 4a) increases over the one at 3054 cm^{-1} (aromatic C–H stretch) in Figure 4b,c. A strong band at 821 cm^{-1} appears after curing (Figure 4b,c); it is attributed to the C–H bend mode of a trisubstituted ethylene. The sharp, intense band at 1230 cm^{-1} (C–O

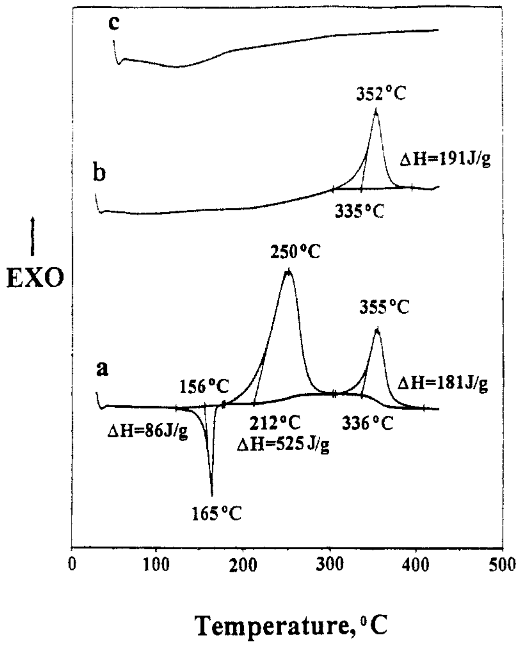

Figure 3. DSC thermograms of 2: monomer (a); after heating to 290 °C at 15 °C/min in the absence of air (b); after heating to 290 °C at 10 °C/min and held for 3 h at 290 °C in the absence of air (c). (The DSCs were recorded in N_2).

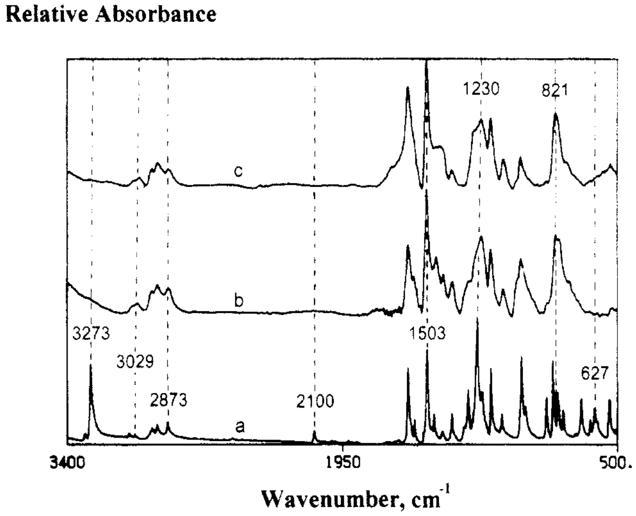

Figure 4. IR spectra of 2: monomer (a); after heating to 290 °C at 15 °C/min in the absence of air (b); after heating to 290 °C at 10 °C/min and held for 3 h at 290 °C in the absence of air (c).

stretch of the benzyl phenyl ether bond) in Figure 4a becomes broader in Figure 4b,c because the monomer is crystalline while the resulting polymer is amorphous. Although this band broadens from Figure 4a through Figure 4c, its integrated area does not change relative to the band at 1503 cm^{-1} (C=C aromatic stretch). There was no evidence to show that much cyclotrimerization had occurred. Glaser type polymerization did not take place since the Raman spectrum (Figure 5b) shows no absorption band in the ethynyl region. The DSC, IR, and Raman data imply that the initial polymerization of the ethynyl groups generated a polyene structure.

Since a polymer with no acetylenic groups is obtained when the monomer has passed through its first exotherm (Figures 3b, 4b, and 5b), the second DSC exotherm must be attributed to other reactions such as further coupling of the polyene chains (postcuring). As far as we can tell, the major structure produced during the polymerization is the polyene.

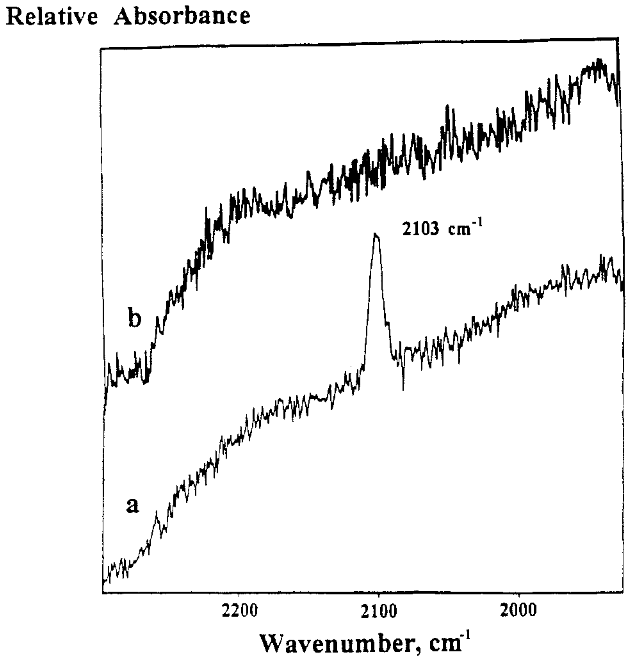

Figure 5. Raman spectra of 2: monomer (a); after heating to 290 °C at 5 °C/min in the absence of air (b).

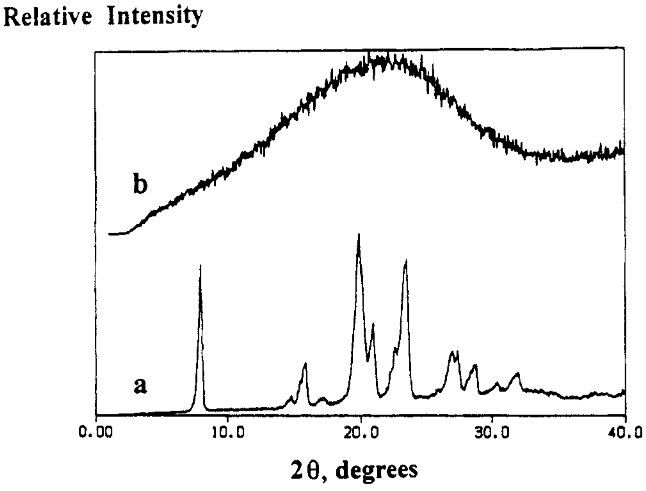

Figure 6. WAXD spectra of 1 (a) and its corresponding polymer (b).

Table 2. Densities (g/cm^3) of 1–6 and 1p–6p

sample	monomer	polymer
1	1.15	1.18
2	1.18	1.19
3	1.29	1.32
4	1.18	1.21
5	1.25	1.27
6	1.21	1.23

Density. The densities of **1p–6p** varied from 1.18 to 1.32 g/cm^3. Their values are listed in Table 2. The densities of the corresponding monomers are also listed. All cross-linked resins had higher densities than their monomers.

Thermomechanical Properties. All cured resins were amorphous. Figure 6 shows the WAXD spectra of monomer **1** and its polymer **1p** as an example. It can be seen that **1p** is completely amorphous. The T_g of the resins could not be detected by DSC, even though samples were cycled between 420 °C and room temperature three times, probably because **1p–6p** were cross-linked and the change in C_p was very small.

Well-consolidated, void-free films of polymers **2–4** were obtained by gradual heating of the monomers on a glass

Table 3. Thermal and Thermooxidative Stability of 1p–6p

	in nitrogen			in air	
polymer	IDT[a] (°C)	MDT[b] (°C)	Y[c] (%)	IDT (°C)	MDT (°C)
1p	410	543	66	407	543
2p	406	542	65	408	548
3p	389	524	61	388	556
4p	401	525	70	400	516
5p	395	515	71	410	552
6p	398	551	65	398	498

[a] Initial decomposition temperature derived by extrapolation. [b] Maximum decomposition temperature. [c] Char yield at 800 °C.

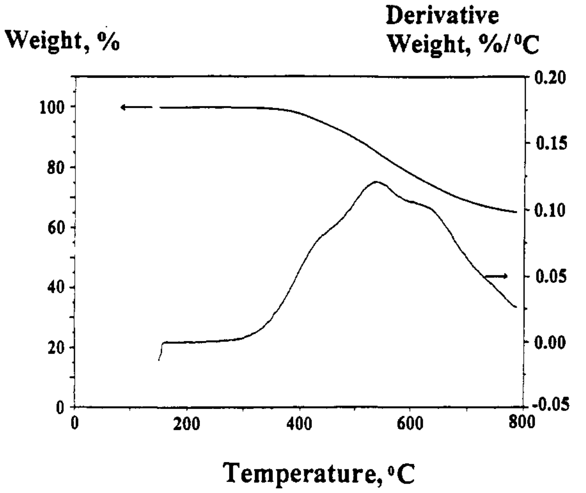

Figure 7. TGA thermogram of the cross-linked polymer **1p** under N_2.

plate in a hot-stage apparatus. Thermomechanical analysis (TMA) was used to evaluate the T_g's and the linear thermal expansion of the polymers. Using an expansion probe at 10 °C/min in static air (TMA), the T_g's of **4p** and **5p** were evaluated as the temperature where the polymer stops expanding linearly as it is heated from room temperature to 500 °C. TMA studies showed that **4p** and **5p** had T_g's of 364 and 330 °C. These polymers have T_g's comparable to polymers derived from polymerization of bis[4-(3-ethynylphenoxy)phenyl] sulfone or acetylene-terminated phenylquinoxalines whose T_g's[1] varied from 300 to 365 °C, the highest reported in the literature in acetylene-terminated polymers. The linear thermal expansions for **4p** and **5p** from room temperature to their T_g's were measured with TMA and were found to be 1.2 and 1%, respectively (expansion coefficients of 4.4×10^{-5} and 2.9×10^{-5} cm/(cm K))! Monomers **1**–**6** melt to low-viscosity liquids, and some of them have a wide processing window. Their polymers have high T_g's and very low linear thermal expansion. They show promise as composite matrices.

Thermogravimetric Analysis. Dynamic thermogravimetric analysis (TGA) is the most favored technique for the rapid evaluation of the thermal stability of polymeric materials. It is especially useful for comparing and ranking the thermal stabilities of different polymers. The TGA data for the resins are listed in Table 3. A TGA thermogram representative of this series of polymers is shown in Figure 7. The polymers exhibited an initial decomposition temperature (IDT) between 388 and 410 °C under both N_2 and air (Table 3). (The IDT is the intersection of the extrapolation of the initial base line and the steepest slope line. Usually, weight loss starts somewhat below this temperature.) In nitrogen their maximum decomposition temperature (MDT) was between 515 and 551 °C, and the anaerobic char yield at 800 °C was between 61 and 71%. Comparing polymers **1p** and **2p**, it can be seen that the existence of a second benzyl phenyl ether bond in the structure of **2** did not significantly influence the thermal or thermooxidative stability. The benzyl phenyl ether bond has not been incorporated in heat-resistant polymers because it was expected to be thermally unstable. The fact that the polymers had an IDT between 389 and 410 °C and a unusually high anaerobic char yield (up to 71%) was attributed to the high cross-link density of their networks which successfully stabilizes this series of resins. Combining data from Tables 1 and 3, it can be seen that **3** and **6** showed low values of enthalpy of polymerization; after their thermal curing they had the lowest thermal and thermooxidative stability. All resins pyrolyzed in air almost completely by 600 °C.

Another interesting feature of these cross-linked polymers was their very high anaerobic char yield compared to polymers of similar chemical structure, linear poly(benzyl phenyl ethers).[20] The fire retardancy[21] of polymers has been correlated to the pyrolysis residue because the surface of the burning polymer serves as a heat shield to retard further decomposition of the polymer, thus increasing the heat and fire resistance of the polymer. Similarly, the residue has been related to the limiting oxygen index (LOI)[21] which is a measure of the fire resistance of a polymer. An approximately linear correlation exists between the char yield at high temperatures (800 °C) and flame retardancy measured by LOI. Van Krevelen[21] has pointed out that polymers which exhibited a high anaerobic char yield also possessed flame retardancy. Thus, these resins are expected to show heat and fire resistance.

Summary and Conclusions

EBEs melt-polymerized; their DSC thermograms showed two intense exotherms. It was demonstrated that the first DSC exotherm was due to the polymerization of the acetylenic groups to form a polyene system. The second exotherm is probably due to further reaction of the polyene chains. **1** and **4** showed wide processing windows of 55 and 40 °C, respectively, which is an attractive processing feature.

The cross-linked EBE resins showed an unusually high anaerobic char yield at 800 °C (61–71%) which indicates that EBE resins may have a high fire retardancy. Since (1) the EBEs have low densities and some of them possess a wide processing window (readily processable materials) and (2) their polymers have very high T_g's plus low linear thermal expansion and good thermal stability, it is expected that these materials could be candidates for high-temperature, light-weight composite matrices.

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