Macromolecules **1996,** *29,* 1073−1075 **1073**

Novel Reactive Cyclobutenedione in Poly(arylene ether) Synthesis

Zhi Yuan Wang* and Laurence Suzzarini

Ottawa-Carleton Chemistry Institute, Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario, Canada K1S 5B6

Received August 22, 1995

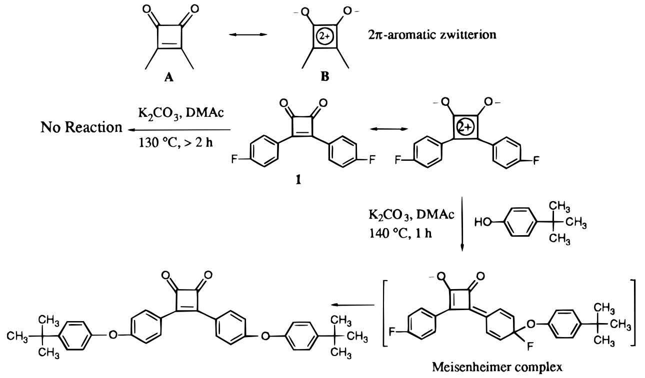
Revised Manuscript Received November 27, 1995

Poly(arylene ether)s (PAEs) comprise a class of polymers generally having arylene or heteroaromatic units which are linked together by ether and other functional groups such as ketone and sulfone. In addition to being functional groups in PAEs, the ketone and sulfone serve as the activating group for the dihalide monomer used in aromatic nucleophilic substitution polymerizations. As one common approach to new PAEs, many electron-withdrawing groups such as amide,[1] quinoxaline,[2] oxadiazole,[3] thiadiazole,[4] and triazole[5] have been developed into the dihalide monomers. The functional group transformation performed on PAEs also represents a unique route to new PAEs with novel structures. This method is useful, especially when the target polymers cannot be synthesized or are difficult to synthesize using conventional polymerization methods due to the lack of suitable reactive monomers. For example, conversion of 1,2-diacylbenzene and 2,2′-diacylbiphenyl units in PAEs into phthalazine and phenanthrene units, respectively, resulted in the formation of new PAEs with higher glass transition temperatures (T_g), improved thermal stabilities, and significantly different viscosities.[6] Chemical transformation of the 1,2-diketone (e.g., benzil) moiety in PAEs to a pyridyltriazine unit afforded polymers with higher T_gs and improved adhesion properties.[7] Furthermore, a series of copolymers could be produced by varying the degree of functional group transformation.[6c] Conceivably, a wide spectrum of new PAEs can be made available from a single dihalide monomer if its functional group serves a dual role as the activating unit for the halide displacement and the reactive site for further polymer transformation.

The 3-cyclobutene-1,2-dione moiety (**A**) can be considered to be the cyclic form of the electron-withdrawing conjugated 1,2-diketone, whose principal resonance structure **B** represents a 2π-aromatic carbocyclic system (Scheme 1).[8] Due to high ring strain, it is labile to heat and light. The cyclic diketone can open upon thermolysis or photolysis to yield a highly reactive bisketene which may enter a wide range of reactions such as Diels−Alder cycloaddition, dimerization, and coupling with alcohols.[8] Thus, the unit **A** (or **B**) could be used as an activating group for the dihalide monomer and as a reactive functional group for further polymer transformation. In this paper, we report the synthesis, polymerization, and transformation of PAEs containing a reactive cyclobutenedione unit.

A simple dihalide monomer containing a cyclobutenedione moiety is 3,4-bis(4-fluorophenyl)-3-cyclobutene-1,2-dione (**1**). It was easily synthesized by Fridel−Crafts reaction of fluorobenzene and squaric acid.[9] The reactivity of monomer **1** toward nucleophilic substitution reaction is quite high according to NMR studies, in comparison with known difluoride monomers such as 4,4′-difluorobenzophenone and 4-fluorophenyl sulfone. The aromatic protons ortho to the cyclobutenedione moiety in **1** have a chemical shift of 8.11 ppm, which is higher than that (7.90 ppm) of the protons ortho to the keto group in 4,4′-difluorobenzophenone. This implies that the whole of the cyclobutenedione moiety provides more electron-withdrawing power than the single keto group. ^{19}F NMR spectroscopy has recently been used to probe the reactivity of difluoride monomers in aromatic nucleophilic substitution reactions.[2,10] The fluorine in **1** appears at −104.15 ppm, indicating again the higher reactivity of monomer **1** than 4,4′-difluorobenzophenone ($\delta_F = -106.01$ ppm) toward nucleophiles.[11]

Scheme 1. Activation by a 2π-Aromatic Carbocyclic Zwitterion System and Model Reactions with Monomer 1



To demonstrate the feasibility of nucleophilic displacement of the fluorine in **1** as a result of activation of the cyclobutenedione group, a model reaction was carried out using 4-*tert*-butylphenol (Scheme 1). The corresponding product, 3,4-bis[4-(4-*tert*-butylphenoxy)phenyl]-3-cyclobutene-1,2-dione isolated in 78% yield, was formed in 1 h at 140 °C in *N,N*-dimethylacetamide (DMAc).[12] In general, nucleophilic substitution reactions of common difluorides in DMAc, NMP, or sulfolane require temperatures ranging from 160 to 220 °C to effect the fluorine displacement.[13] Such an ease in the fluorine displacement of **1** strongly suggests that the activation also comes from the fully positive-charged resonance component (Scheme 1). This zwitterion system makes the fluorobenzene moiety more acceptable for nucleophilic attack, thus significantly enhancing the reaction rate for the Meisenheimer complex formation. The nucleophilic displacement of the fluorine in **1** is also chemically specific toward a phenoxide nucleophile. In a control experiment, treatment of **1** in DMAc with 1 mol equiv of potassium carbonate at 130 °C for more than 2 h did not yield any hydrolyzed products or other ring-opening products (Scheme 1). The difluoride **1** was recovered and reconfirmed by spectroscopic means.

Following the model reaction, polycondensations of **1** with some commercially available bisphenols, 4,4′-isopropylidenediphenol (BPA), 4,4′-(hexafluoroisopropylidene)diphenol (6F-BPA), 9,9-bis(4-hydroxyphenyl)fluorene, and phenolphthalein, were performed (Scheme 2). In all cases, bisphenoxide salts were prepared first using potassium carbonate in DMAc, followed by the addition of monomer **1**. All polymerizations proceeded readily at 130 °C and produced polymer gels in less than 1 h. Except for polymer **2a** derived from BPA, the gels can be completely dissolved by adding more DMAc and some acetic acid. The gels could not be re-formed from the isolated polymers when treated under similar polymerization conditions. The gelation might be caused by cross-linking, due to the ester bond formation via the possible reaction between the cyclobutenedione moiety

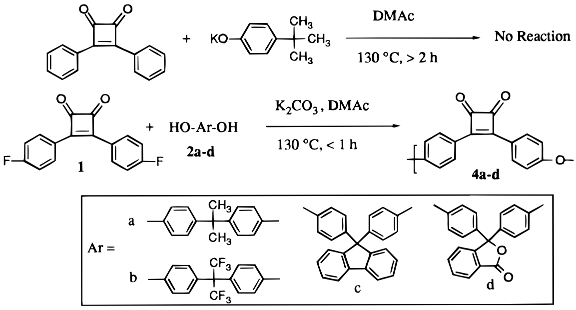
0024-9297/96/2229-1073$12.00/0

Table 1. Characterization of Homopolymers 4a–d

polymer	M_n[a]	M_w[a]	η[b] (0.5 g/dL)	η[b] (0.125 g/dL)	T_d,[c] °C
4a	gel		N/D[d]	N/D	N/D
4b	1830	5190	0.35	0.78	372
4c	2170	5750	0.34	5.72	406
4d	N/D	N/D	0.68	0.63	340

[a] Measured by GPC relative to polystyrene standards. [b] Inherent viscosity in DMAc at 25 °C. [c] Onset temperature for 5% weight loss, as assessed by TG at 10 °C/min under nitrogen. [d] Not determined.

Scheme 2. Control Reaction and Polymerization of Monomer 1



and the nucleophilic phenoxide. However, this possibility has been ruled out. As a model reaction (Scheme 2), heating 3,4-diphenyl-3-cyclobutene-1,2-dione with potassium *tert*-butylphenoxide in DMAc at 130 °C for more than 2 h did not produce any ring-opening products. Two starting compounds were recovered, as characterized by NMR. Therefore, only noncovalent bonding appears to be responsible for the observed gelation. Although the exact nature of the noncovalent bonding is still uncertain, the polarizable cyclobutenedione unit appears to play an important role. It is likely that the ionic bonding between the charged intermediate or the zwitterion which is present favorably in the basic medium causes the interchain interactions. Upon acidification, neutral cyclobutenedione is regenerated from the zwitterionic form, thus breaking any ionic interchain bonding. The polymerization was also attempted in the solvents that could dissolve the polymer gels. In pyridine or 2,6-lutidine, no polymerization occurred. In DMAc or DMF, the polymerization took place but resulted in gelation even under the high dilution condition (5%). The addition of lithium chloride (15 mol %) had no effect on preventing the gelation. A higher dose of lithium chloride (7 mol equiv) completely inhibited the nucleophilic substitution polymerization. All polymers were obtained as yellow powders and formed brittle films when cast from the chloroform solution. GPC measurement indicated that PAEs **4b–d** were of low molecular weights relative to polystyrene (Table 1). PAEs **4b** and **4c** behaved like ionic polyelectrolytes in solution. At the concentration of 0.5 g/dL, inherent viscosities were in the vicinity of 0.35 dL/g (DMAc, 25 °C). At a more dilute concentration (0.125 g/dL), the viscosity value increased dramatically up to 5.72 dL/g. A linear dependence of the inherent viscosity on polymer concentration was found for PAE **4d** with the intrinsic viscosity of 0.61 dL/g.

The presence of the cyclobutenedione moiety in the polymer was confirmed by IR and NMR. The IR spectra of all polymers showed a strong peak between 1769 and 1780 cm^{-1}, due to the cyclic ketone. For comparison, the same carbonyl peaks for monomer **1** and the model ether[12] appear at 1766 and 1761 cm^{-1}, respectively. In both proton and carbon NMR spectra, the peaks attributed to the diphenylcyclobutenedione fragment were observed at the expected chemical shifts with correct integration ratios.

The T_gs could not be detected by differential scanning calorimetry (DSC) for all PAEs **4**. Instead, broad exothermic peaks were observed from 200 to 400 °C due to the cyclobutenedione ring opening. After scanning up to 400 °C, there were no more detectable exotherms in the second DSC runs. For all PAEs **4**, the weight loss began at 200 °C, in accordance with the onset ring-opening temperatures, as assessed by thermogravimetry (TG). It is known that the cyclobutenedione ring can open to form a highly reactive bisketene upon thermolysis and further yields the acetylene by ejecting two molecules of carbon monoxide at elevated temperatures.[14] Similarly, the loss of carbon monoxide from the cyclobutenedione unit in PAEs **4** was confirmed by using the combined TG–IR technique. It was found that PAEs **4** gradually released carbon monoxide, starting at 295 °C and continuing until the catastrophic decomposition temperature of 500 °C.

Incorporation of a small amount of reactive cyclobutenedione unit into poly(arylene ether sulfone) was further investigated. Both random and sequential copolymerizations of **1** with 4-fluorophenyl sulfone were carried out using 25 mol % of monomer **1** in the feed. When two difluoride monomers and 6F-BPA were mixed together and polymerized randomly, the resulting polymer had a low molecular weight and displayed a multimodal GPC trace. However, when monomer **1** was introduced into the reaction system after the oligomers had been formed from 4-fluorophenyl sulfone and 6F-BPA, copolymer **5** had a higher molecular weight. During sequential polymerization, multiple peaks at a longer elution time in GPC, due to the oligomers, became a single peak at a shorter elution time shortly (<10 min) after the addition of monomer **1**. Although the gelation occurred as well, copolymer **5** was redissolved in DMAc/acetic acid and isolated as small yellowish fibers. Copolymer **5** had a high molecular weight (M_w = 39 000, M_n = 20 200) and a high intrinsic viscosity (0.97 dL/g in $CHCl_3$ at 25 °C). The actual cyclobutenedione content or unit x in **5** was determined by ^1H NMR to be 21%. The copolymer exhibited good solubility in many common organic solvents such as chloroform, 1,1,2,2-tetrachloroethane (TCE), DMAc, DMSO, THF, and acetone.

The T_g of **5** was found to be 217 °C by DSC (Figure 1, trace b), which is slightly higher than that (199 °C) of the homopolysulfone without the cyclobutenedione unit. DSC also showed a broad exothermic peak ($\Delta H = -6.4$ mJ/mg) ranging from 250 to 340 °C on the first scan (Figure 1, trace a) up to the temperature (450 °C) for 5% weight loss in nitrogen. The second DSC scan displayed a flat trace with no sign of any transitions, suggesting the cross-linking occurred during the first run. The cross-linking can be caused by various modes of couplings between reactive bisketenes and/or the acetylenes produced after ejecting two molecules of carbon monoxide.

Finally, substituted cyclobutenedione is known to react thermally or photochemically with alcohols to give the corresponding diesters.[15] The model reaction of 3,4-diphenyl-3-cyclobutene-1,2-dione[16] with an excess of *n*-octanol at 180 °C afforded the expected di-*n*-octyl 2,3-diphenylsuccinate (Scheme 3).[17] The same transformation was then performed on copolymer **5**. Simply heating the polymer in an excess of *n*-octanol and a small amount of TCE as a cosolvent at 160 °C smoothly converted the cyclic diketone into the acyclic diester

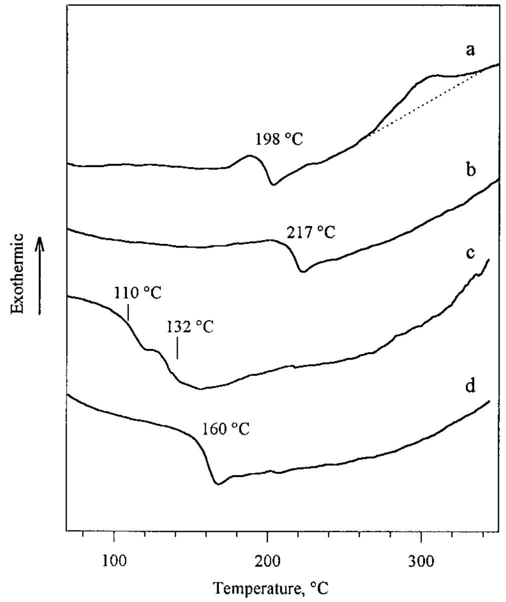
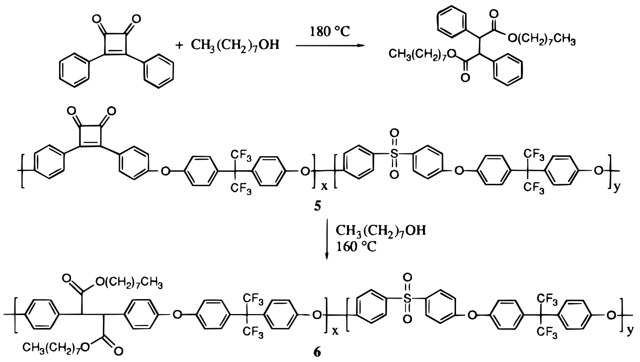


Figure 1. DSC (10 °C/min, under nitrogen) traces of (a) **5**, first scan; (b) **5**, second scan; (c) **6**, first scan; (d) **6**, second scan.

Scheme 3. Model Transformation and Transformation of Copolymer 5



(Scheme 3). GPC showed a single trace for the "as-made" **6** with the calculated molecular weight of 32 300 relative to polystyrene, thus indicating no chain cleavage during polymer transformation. From the ^{1}H NMR spectrum, 20% diester units (x) were found in **6** by integration, which corresponds to the ratio of the cyclobutenedione unit in the parent polymer. This clearly proves complete functional group transformation. IR analysis also showed the disappearance of the carbonyl band at 1776 cm^{-1} and the appearance of a new peak at 1734 cm^{-1} due to the ester group. Exothermic ring opening was not observed for polymer **6** at elevated temperature in the first DSC scan (Figure 1, trace c), due to the nil content of the cyclobutenedione units. As expected, polymer **6** had a lower T_g of 160 °C (Figure 1, trace d) compared to **5**. In addition to being soluble in the solvents that dissolved **5**, polymer **6** was also very soluble in toluene because of a long aliphatic side chain.

In conclusion, a new type of activating group having a charged 2π-aromatic carbocyclic zwitterion structure has been shown with novel monomer **1**. As demonstrated in thermal ring-opening reaction with alcohol to form the ester, the cyclobutenedione group can serve as a reactive lateral or end group for cross-linking with diols or polyols. The work on curing high-performance PAEs containing reactive cyclobutenedione end groups is ongoing.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

References and Notes

(1) Hedrick, J. L. *Macromolecules* **1991**, *24*, 812.
(2) (a) Hedrick, J. L.; Labadie, J. W. *Macromolecules* **1990**, *23*, 1561. (b) Hedrick, J. L.; Twieg, R.; Matray, T.; Carter, K. R. *Macromolecules* **1993**, *26*, 4833.
(3) (a) Hedrick, J. L.; Twieg, R. *Macromolecules* **1992**, *25*, 2021. (b) Johnson, R. N.; Farnham, A. G.; Clendinning, R. A.; Hale, W. F.; Merriam, C. N. *J. Polym. Sci., Part A-1* **1967**, *5*, 2375.
(4) Saegusa, Y.; Iwasaki, T.; Nakamura, S. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 249.
(5) Carter, K. R.; Jonsson, H.; Twieg, R.; Miller, R. D.; Hedrick, J. L. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1992**, *33* (1), 388.
(6) (a) Singh, R.; Hay, A. S. *Macromolecules* **1992**, *25*, 1025. (b) Zhang, C.; Wang, Z. Y. *Macromolecules* **1993**, *26*, 3330. (c) Wang, Z. Y.; Zhang, C.; Arnoux, F. *Macromolecules* **1994**, *27*, 4415.
(7) Strukelj, M.; Hedrick, J. C. *Macromolecules* **1994**, *27*, 7511.
(8) (a) Tidwell, T. T. *Ketenes*, John Wiley & Sons: New York, 1995. (b) Also see the recent review and references cited therein: Allen, A. D.; Ma, J.; McAllister, M. A.; Tidwell, T. T.; Zhao, D.-C. *Acc. Chem. Res.* **1995**, *28*, 265.
(9) A 100 mL round-bottomed flask equipped with a condenser was flame dried under nitrogen. This flask was charged with squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) (18.20 g, 0.160 mol), thionyl chloride (25.5 mL, 0.353 mol), fluorobenzene (80.0 mL), and 4 drops of DMF. The solution was heated at reflux until a clear brown solution was formed. After cooling to 0 °C with an ice bath, aluminum chloride (47.23 g, 0.354 mol) was slowly added. The solution was then allowed to warm up to 60 °C and held at this temperature for 36 h. The reaction solution was cooled to room temperature and extracted with chloroform (2 × 100 mL). The organic phase was dried and concentrated *in vacuo*. The residual product was then recrystallized twice from methanol, giving the pure monomer **1** as yellow needles: 27.20 g (63%); mp 175−177 °C; IR (KBr, cm^{-1}) 1766 (CO); ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.11 (4 H, q), 7.27 (4 H, t); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.17, 186.00, 168.39, 163.32, 131.54, 131.36, 125.28, 125.14, 117.47, 117.03; ^{19}F NMR (282.23 MHz, DMSO-d_6) δ −104.15 (relative to CCl_3F) or −102.78 (in $CDCl_3$, relative to CCl_3F); HRMS Calculated for $C_{16}H_8O_2F_2$: 270.0490, Found: 270.0494.
(10) Hedrick, J. L.; Jonsson, H.; Carter, K. R. *Macromolecules* **1995**, *28*, 4340.
(11) ^{19}F NMR experiments were performed on dilute solution in DMSO-d_6 and the chemical shifts are reported in ppm relative to CCl_3F with the chemical shift of 0 ppm. The smaller the negative chemical shift is, the higher the positive charge density is on the carbon bearing the fluorine or the more reactive the monomer is.
(12) 3,4-Bis[4-(4-*tert*-butylphenoxy)phenyl]-3-cyclobutene-1,2-dione: mp 142 °C; IR (KBr, cm^{-1}) 1761 (C=O); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.35 (s, 18 H), 7.05 (t, 18 H), 7.34 (d, 4 H), 8.08 (d, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.74, 34.78, 117.98, 120.22, 122.70, 127.27, 130.69, 148.35, 152.71, 162.80, 184.80, 184.99, 196.43; MS (EI, *m/e*, relative intensity (%)) 530 ($M^{\bullet+}$, 1.4), 474 ($M^{\bullet+}$ − 2 CO, 10.4), 459 (474 − $^{\bullet}CH_3$, 4.9), 119 (100).
(13) Strukelj, M.; Hedrick, J.; Hedrick, J.; Tweig, R. *Macromolecules* **1994**, *27*, 6277.
(14) (a) Bock, H.; Ried, W.; Stein, U. *Chem. Ber.* **1981**, *114*, 673. (b) Eggerding, D.; West, R. *J. Am. Chem. Soc.* **1976**, *98*, 3641. (c) Chickos, J. S. *J. Org. Chem.* **1973**, *38*, 3642. (d) Rubin, Y.; Lin, S. S.; Knobler, C. B.; Anthony, J.; Boldi, A. M.; Diederich, F. *J. Am. Chem. Soc.* **1991**, *113*, 6943.
(15) (a) Bloomquist, A. T.; Lalancette, E. A. *J. Am. Chem. Soc.* **1961**, *83*, 1387. (b) Obata, N.; Takizawa, T. *J. Chem. Soc., Chem. Commun.* **1971**, 587.
(16) Green, B. R.; Neuse, E. W. *Synthesis* **1974**, 46.
(17) Di-*n*-octyl 2,3-diphenylsuccinate: mp 90−92 °C; IR (KBr, cm^{-1}) 1720 (C=O), 1210 (C−O); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, 6 H), 1.20 (m, 24 H), 3.80 (m, 4 H), 4.38 (s, 2 H), 7.30 (t, 4 H), 7.37 (m, 2 H), 7.50 (dd, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.40, 22.93, 25.85, 28.60, 29.32, 29.37, 32.04, 55.43, 65.22, 128.14, 128.74, 128.88, 136.76, 171.82; MS (EI, *m/e*, relative intensity (%)) 494 ($M^{\bullet+}$, 1.6), 364 ($M^{\bullet+}$ − $^{\bullet}CH_3(CH_2)_6CH_2OH$, 44), 252 (100); HRMS Calculated for $C_{32}H_{46}O_4$: 494.3384, Found: 494.3418.

MA951234J