containing a single solvent. For a mixture of oligomers with small differences in chlorine end groups, but very similar boiling points and molecular weights, the affinities for the PTFE polymer as well as the refractive index of those oligomers could be comparable. We used two different boiling fractions of the MO solvent and obtained essentially the same molecular weight. Figure 2 shows a typical Zimm plot with $M_w = (2.9 \pm 0.2) \times 10^5$ g/mol (or dalton), $A_2 = -(6.7 \pm 1.3) \times 10^{-5}$ mol cm^3 g^{-2}, and $R_g \approx 17.8 \pm 2.4$ nm. The negative A_2 suggests that the MO solvent is a poor solvent for PTFE at 340 °C. Figure 3 shows a typical net intensity–intensity time correlation function. We first tried to examine the clarified oligomers at 340 °C and were satisifed with a lack of angular dissymmetry in intensity measurements and a lack of correlations over the entire correlator delay time range. From a simple cumulants analysis,[12] we note that the polydispersity index[13] is high, with $M_z/M_w \sim 2$. A detailed characterization is under way.

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Registry No. PTFE, 9002-84-0; MO, 9002-83-9.

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Cyclobutene-Containing Monomers and Polymers. Polymerization and Cross-Linking via Thermally Generated Butadiene Units

New monomers and polymers have been synthesized that contain 1,2-disubstituted cyclobutene moieties capable of thermal ring-opening to 2,3-disubstituted butadiene groups. Model diamides and polyamides are described here.

The 1,2-cyclobutenedicarboxylic acid intermediate **1** was synthesized via the dicyano compound by published procedures.[1,2] The diacid chloride **2** was readily obtained with thionyl chloride.[3] Conversion of **2** to the N-substituted diamides **3–5** took place in good yield.[4] The diamides serve

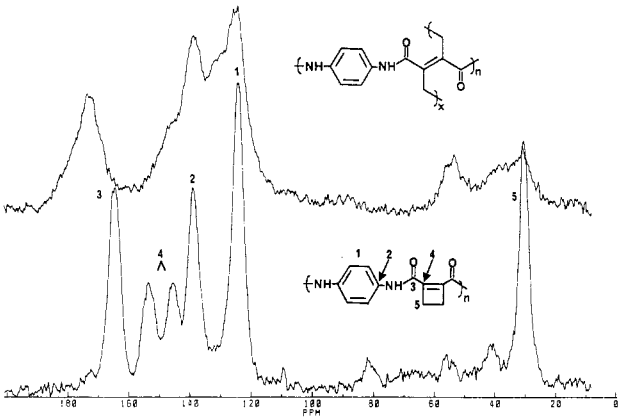
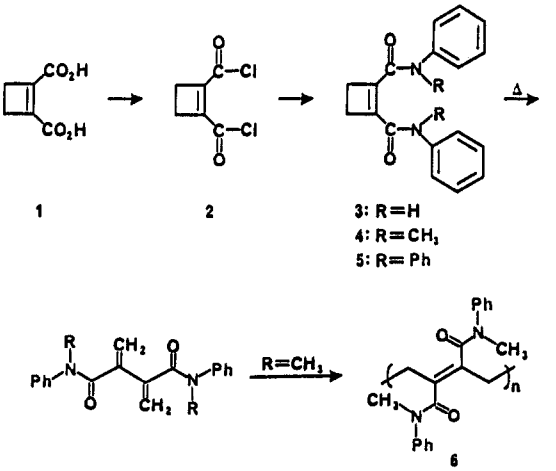


Figure 1. Cross-polarization/magic angle spinning ^{13}C NMR spectra of the cyclobutene-containing polyamide (lower trace) and its thermolysis product (upper trace).

both as models for aromatic polyamides and as precursors for a new family of disubstituted polybutadienes.



Previous work has focused mainly on the cycloaddition chemistry of several cyclobutenes and their butadiene derivatives.[5] Two reports have appeared, however, on the spontaneous polymerization of ring-opened compounds. Thermolysis of 1,2-dicyanocyclobutene gave a soluble polymer of undetermined structure,[3] while polyolefins containing cyclobutene units in their backbone became insoluble after thermolysis.[6] We have found that polymerization and cross-linking are also possible for other 1,2-disubstituted cyclobutenes and their polymers.

Thermolysis of the model diamides was monitored by DSC. All three compounds displayed melting endotherms followed by broad reaction exotherms over the range 200–250 °C with maxima of 210–220 °C. Thermolysis of **4** led directly to polybutadiene **6** (proposed structure; 1,2 incorporation is also possible), which was soluble in common organic solvents.[7] Further work is under way on the general polymerizability of the butadienes and on characterization of the monomers and polymers.

We have also synthesized polyamide **7** from **1** and *p*-phenylenediamine using a mild triphenylphosphine–hexachloroethane procedure.[8] Figure 1 shows the ^{13}C CP/MAS spectra of this polymer and its insoluble thermolysis product (proposed structure **8** leading to **9**). The changes in chemical shifts for the amide carbonyl and the alkene carbons are consistent with solution spectra for model diamides except that the solid polyamide shows *two* peaks for the alkene carbons. This may be due to restricted rotation caused by intramolecular hydrogen bonding that forces the two cyclobutene alkene carbons into different chemical environments.

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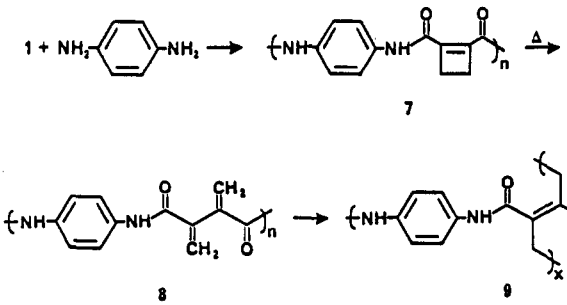

While we have indicated a crosspolymerization structure for **9**, it is also possible for cycloadditions to lead to cross-linked and insoluble product. Additional polyamides are being synthesized, and their thermolysis chemistry and characterization are under further study.

These systems offer the unique ability to generate new polybutadienes from the model diamides. More important is the potential of cyclobutene-containing polymers to function as thermally cross-linkable components of composites and high-performance polymers.

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Novel Synthesis of High Molecular Weight Aramids from N-Silylated Aromatic Diamines and Aromatic Diacid Chlorides

Wholly aromatic polyamides (aramids) are among the oldest members of the class of thermally stable polymers, and some of them have been commercialized as high temperature resistant fibers, high-strength and high-modulus fibers, and high-performance plastics.[1] These aramids are usually prepared through the conventional diamine–diacid chloride route shown in eq 1 by either an interfacial or a low-temperature solution method.[2]

$$H_2N\text{–Ar–}NH_2 + ClOC\text{–Ar'–}COCl \xrightarrow{-HCl} [\text{–NH–Ar–NHC(O)–Ar'–C(O)–}]_n \quad (1)$$

Recently, we found that N-trimethylsilylated aromatic amines were far more reactive than the corresponding unsubstituted amines toward acid chlorides, giving excellent yields of amide compounds. The unusually high reactivity of N-silylated amines toward acid chlorides was entirely unexpected,[3] though N-trimethylsilylated aromatic diamines were prepared many years ago for the synthesis of polyamines[4] and polyureas.[5]

We now wish to communicate a novel and facile synthesis of aramids with high molecular weights by the low-temperature solution polycondensation of N-trimethylsilylated aromatic diamines (I) with aromatic diacid chlorides (II) (eq 2). Silylated diamines Ia and Ib were

$$Me_3SiNH\text{–Ar–}NHSiMe_3 + ClOC\text{–Ar'–}COCl \xrightarrow{-Me_3SiCl} [\text{–NH–Ar–NHC(O)–Ar'–C(O)–}]_n \quad (2)$$

Ia, Ar = *m*-C_6H_4 IIa, Ar' = *m*-C_6H_4
Ib, Ar = *p*-C_6H_4 IIb, Ar' = *p*-C_6H_4

synthesized by the reaction of the corresponding diamines with trimethylsilyl chloride in the presence of triethylamine. Both Ia and Ib were purified by distillation: Ia, bp 88–89 °C (0.5 Torr);[5] Ib, bp 150–152 °C (8 Torr), mp 102–104 °C.[5]

A typical polymerization procedure is as follows: In a flask 1.263 g (5 mmol) of *N,N'*-bis(trimethylsilyl)-*p*-phenylenediamine (Ib) and 1.33 g of lithium chloride were dissolved in 16.7 mL of hexamethylphosphoramide (HMPA) and 8.3 mL of *N*-methyl-2-pyrrolidone (NMP). The solution was brought to −15 °C using an ice–salt mixture, and 1.015 g (5 mmol) of powdered terephthaloyl chloride (IIb) was added. The mixture was stirred at −10 to −5 °C under nitrogen. The polymerization proceeded in a homogeneous solution and the solution became a gel after 6 h. The reaction mixture was worked up by agitating with methanol. The polymer was collected by filtration, washed thoroughly with hot methanol, and dried at 80 °C in vacuo. The polymer weighed 1.18 g (99%) and had an inherent viscosity of 7.41 $dL \cdot g^{-1}$, measured at a concentration of 0.5 $g \cdot dL^{-1}$ in concentrated sulfuric acid at 30 °C.

It was confirmed that the low-temperature solution polycondensation proceeded according to eq 2 with elimination of trimethylsilyl chloride to afford aramids having high inherent viscosities.

Reaction conditions were examined in the polycondensation of Ib with IIb giving aramid PPTA (Du Pont's Kevlar molecule). Morgan et al.[6] reported the synthesis of high molecular weight PPTA by the polycondensation of *p*-phenylenediamine with IIb in a mixed solvent of HMPA and NMP. However, in the present investigation, addition of lithium chloride to the HMPA–NMP binary solvent was found to be advantageous, and hence a HMPA–NMP–LiCl mixture was used as the reaction medium.

The effect of reactant concentration on the inherent viscosity of PPTA formed was investigated. It was found that an inherent viscosity greater than 7.0 $dL \cdot g^{-1}$ was readily obtained when the concentration was in the range 0.1–0.2 $mol \cdot L^{-1}$. The lower inherent viscosity obtained at higher reactant concentration is attributable to reduced reactant mobility due to the onset of gelation before high inherent viscosity can be reached.

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