Macromolecules

Volume 24, Number 9 April 29, 1991

New Cross-Linking End Caps for Polyquinoline Prepolymers: Synthesis, Processing, and Thermal Properties

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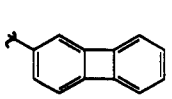
Received June 25, 1990

ABSTRACT: Flexible quinoline oligomers were end-capped with 4-acetylbenzocyclobutene (BCB), 6-acetyl-8-phenyl-1,2-dihydro[3,4]cyclobuta[1,2-*b*]quinoline (CBQ), and 8-acetyl-6b,10b-dihydrobenzo[*j*]cyclobut-[1,2-*a*]acenaphthylene (BCBAN). The oligomers were melt-processed under various conditions. The best conditions afforded high-quality films that exhibited good flexural moduli (E'). Oligomers capped with CBQ and BCBAN gave insoluble cured films of comparable quality under the same cure conditions. The BCBAN-capped oligomer gave a cured film with superior stability by isothermal gravimetric analysis (IGA) in air at 400 °C. All three end caps afforded high cross-link densities at cure temperatures of 234–380 °C. The novel CBQ and BCBAN end caps are conveniently synthesized and stable under ambient conditions, making them attractive for use as new cross-linking groups.

Introduction

In previous efforts to prepare readily processible polyquinoline prepolymers that, upon curing, would give highly cross-linked, thermally stable polymer networks, biphenylene (**1**)[1] and [2.2]paracyclophane (**2**)[2] were examined



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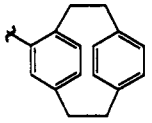

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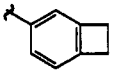

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as cross-linking end caps. Biphenylene end-capped oligomers provided cured films (and composites) possessing thermal stability that was lower than expected based on a consideration of the types of structures generated by the thermolysis of biphenylene in an aromatic medium.[3] Also, it was necessary to utilize a metal catalyst to lower the ring-opening temperature of biphenylene, in order to prevent excessive decomposition during cure.[4] Consequently, we have sought other end-capping agents that would be useful as alternatives to biphenylene.

[2.2]Paracyclophane end caps undergo thermal ring opening in polyquinolines at a much more convenient temperature than biphenylene.[2] Consequently, a metal ring-opening catalyst is not necessary. Unfortunately, the [2.2]paracyclophane end caps afforded cured films that possessed much poorer thermooxidative stability than cured films using biphenylene as the end cap.[2]

Other workers have shown a great deal of interest in the benzocyclobutene ring system **3** as a reactive end group for monomeric and oligomeric cure resin systems.[5] In the present work, we report the synthesis, characterization, curing, and thermal and mechanical properties of polyquinoline oligomers end-capped with benzocyclobutene and two new, related reactive end groups.

Results and Discussion

End-Cap Synthesis and Properties. The functionalized benzocyclobutene (BCB) end cap, 4-acetylbenzocyclobutene (**5**)[6] was produced by a combination of literature techniques,[7] and a method of palladium-catalyzed ethoxyvinylation and hydrolysis[8a] that was recently improved in our laboratories[8b] (Figure 1). It was isolated from the 3-acetyl isomer by multiple recrystallizations.

A related compound, 1,2-dihydro[3,4]cyclobuta[1,2-*b*]-quinoline (**8**), was previously synthesized by the base-catalyzed Friedländer reaction between 2-aminobenzaldehyde (**6**) and cyclobutanone (**7**) (eq 1).[9] Due to the facile synthesis of this benzocyclobutene analogue, it appeared

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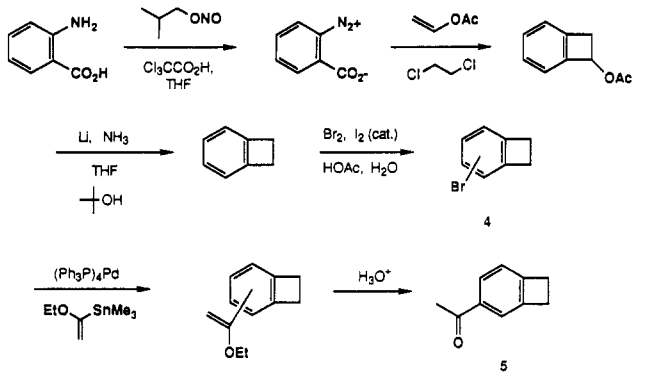


Figure 1. Synthesis of 4-acetylbenzocyclobutene (**5**).

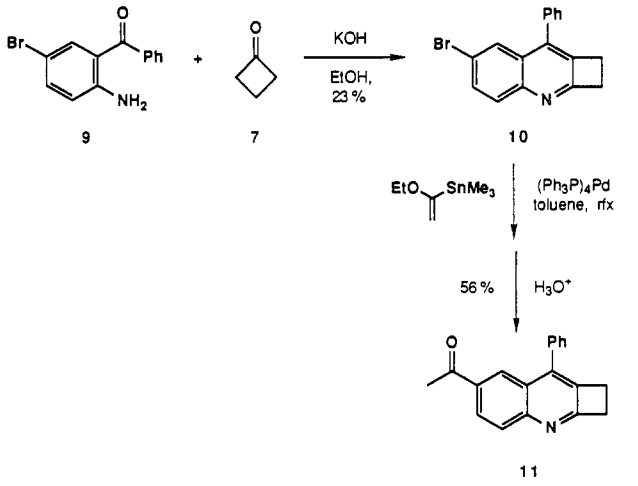
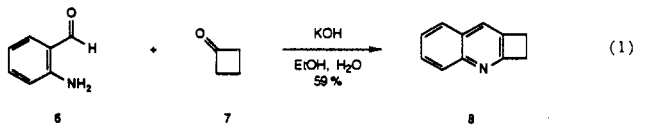


Figure 2. Synthesis of CBQ end cap **11**.

particularly attractive as a possible alternative ring system for use as a cross-linking end cap. Thus, the novel cy-



clobutaquinoline (CBQ) end cap 6-acetyl-8-phenyl-1,2-dihydro[3,4]cyclobuta[1,2-*b*]quinoline (**11**) was produced by the base-catalyzed Friedländer condensation of 2-amino-5-bromobenzophenone (**9**)[10] with cyclobutanone (**7**) followed by the aforementioned palladium-catalyzed ethoxyvinylation and hydrolysis[8] (Figure 2). Intermediate bromide **10** was readily isolated by flash chromatography and purified by recrystallization. Differential scanning calorimetry (DSC) of **10** showed a sharp melting point endotherm at 112 °C and the maximum of the four-membered ring-opening exotherm at 336 °C. Bromide **10** underwent ethoxyvinylation and subsequent hydrolysis, giving complete conversion to end cap **11**. The acetyl compound was readily isolated by chromatography and further purified by recrystallization. DSC of **11** showed a sharp melting endotherm at 164 °C and the maximum of the four-membered ring-opening exotherm at 352 °C. This end cap was more conveniently synthesized than the parent benzocyclobutene end cap **5** and showed greater room temperature stability. Thus, it was expected that **11** would represent a significant improvement over the parent benzocyclobutene, for use as a reactive polymer end group.

The interesting compound 6b,10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (**14**) has been synthesized by the addition of benzyne (**12**) to acenaphthylene (**13**) (eq 2).[11]

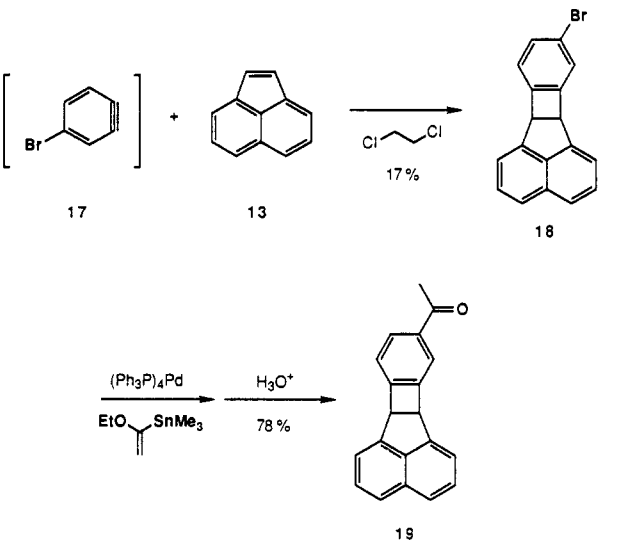
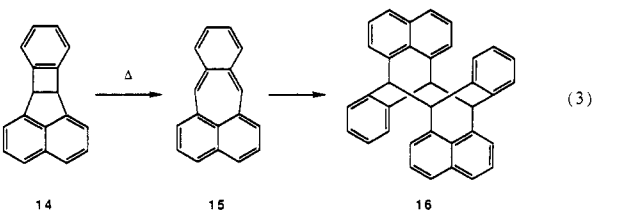


Figure 3. Synthesis of BCBAN end cap **19**.

It has been reported that the four-membered ring of

compound **14** opens above ~200 °C to give highly reactive benzopleiadene **15** (eq 3), which dimerizes in high yield to



compound **16** with no significant side reactions.[11b] Therefore, it was expected that the benzocyclobutacenaphthylene (BCBAN) ring system would be another convenient cross-linking end cap for high-performance polymers.

The [2 + 2] addition of bromobenzyne (**17**)[12] to acenaphthylene (**13**) (Figure 3) gave a 17% yield of bromide **18**, which is higher than the 9.2% yield reported[11a] for the synthesis of the unsubstituted analogue, **14**.[13] Differential scanning calorimetry (DSC) of **18** showed the melting endotherm at 141 °C and the maximum of the ring-opening exotherm at 234 °C.

Compound **18** was converted to acetyl end cap **19**, again by palladium-catalyzed ethoxyvinylation and hydrolysis.[8] DSC showed the melting endotherm at 161 °C, and the maximum of the ring-opening exotherm at 237 °C.

The flexible polyquinoline monomers 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**20**) and 4,4′-diacetyldiphenyl ether (**21**) were prepared according to the standard procedures.[14]

Oligomer Synthesis and Properties. Three oligomeric polyquinolines were prepared by the acid-catalyzed Friedländer polymerization of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**20**) and 4,4′-diacetyldiphenyl ether (**21**) (Figure 4).[1] The stoichiometric balance between the two monomers was controlled in order to obtain a number-average degree of polymerization (DP_n) of 22. The bis(aminoketone) monomer **20** was used in excess, allowing the resulting oligomers to be end-capped with acetylated end caps **5**, **11**, and **19**.

The number-average molecular weights (M_n) of the oligomers were determined by dilute solution viscosity

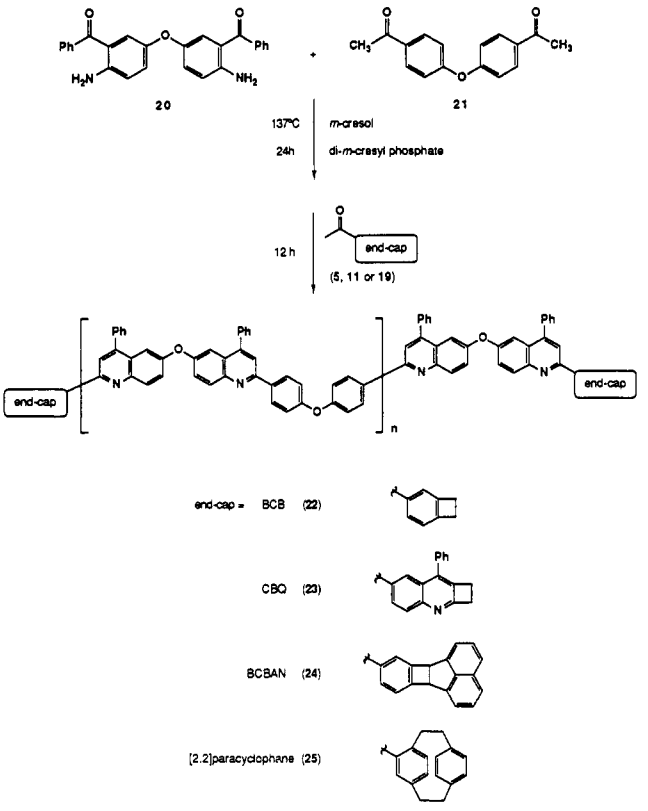


Figure 4. Synthesis of end-capped polyquinoline prepolymers.

Table I
Molecular Weights of End-Capped Oligomers[a]

oligomer	end cap	$[\eta]$	DP_n	M_n
22	BCB	0.526	25	15 600
23	CBQ	0.463	20	12 800
24	BCBAN	0.813	49	30 100

[a] Dilute solution viscosity measurements in $CHCl_3$, $[\eta] = KM_n^a$.

Table II
Differential Scanning Calorimetry of Uncured Oligomers

oligomer	end cap	T_g, °C	Exo_{max}, °C
22	BCB	231	277
23	CBQ	221	397
24	BCBAN	245[a]	238[b]
25[c]	PCP	252	357

[a] Approximate; partially obscured by the ring-opening exotherm. [b] Coincident with the T_g. [c] DP = 22; prepared in previous work.[2]

measurements in chloroform (Table I). The extrapolated intrinsic viscosities were substituted into the Mark–Houwink equation ($K = 9.0 \times 10^{-4}$ and $a = 0.66$ for ether–ether polyquinolines, by membrane osmometry[14a]) to obtain M_n values. A reproducible lack of good linearity was observed in the concentration dependence of reduced and inherent viscosities.

The thermal transitions of the uncured oligomers were determined by differential scanning calorimetry (Table II and Figure 5). The properties of an analogous DP = 22 [2.2]paracyclophane end-capped oligomer (**25**, reported previously[2]) are included for comparison. The cyclophane ring-opening exotherm was observed to be at a maximum just above 350 °C, and this proved to be an ideal cure temperature for oligomeric polyquinolines.[2] DSC of an uncured powder sample of BCB-capped oligomer **22** exhibited the T_g at 231 °C, and the maximum for the ring-opening exotherm (Exo_{max}) occurred at 277 °C. A sample annealed in the DSC sample cup for 30 min at 300 °C showed an increase of 33 °C in T_g to 264 °C. After

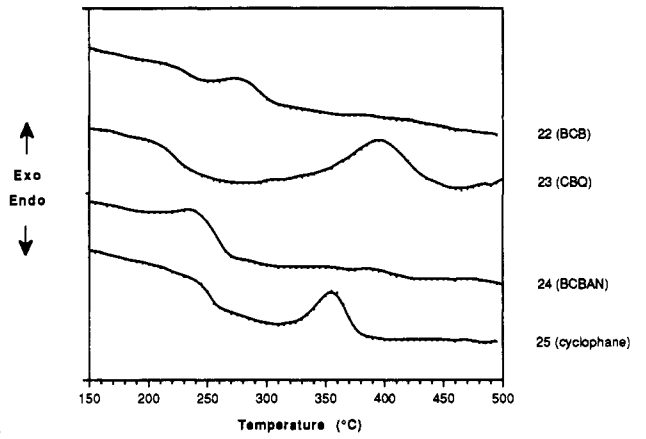


Figure 5. Differential scanning calorimetry of end-capped quinoline oligomers.

annealing, the ring-opening exotherm had completely disappeared, indicating complete thermal curing of the end groups.

DSC of the uncured powder sample of CBQ-capped oligomer **23** showed the T_g at 221 °C and the maximum for the four-membered ring-opening exotherm at 397 °C. This ring-opening temperature was significantly higher than had been observed for the neat end cap and its precursor (vide supra). A sample annealed in the DSC sample cup for 30 min at 350 °C showed an increase in T_g of 47 °C, to 268 °C. The ring-opening exotherm had completely disappeared, indicating complete thermal curing of the end groups.[16]

DSC of the powder sample of BCBAN end-capped oligomer **24** exhibited the T_g at 259 °C, and the maximum of the ring-opening exotherm for the end cap was coincident with the onset of the T_g transition at 238 °C. This precluded an exact determination of T_g. The low ring-opening temperature was expected and closely corresponded with those observed for end cap **19** and its bromide precursor **18** (vide supra).[17] A sample of **24** annealed in a DSC sample cup for 30 min at 300 °C showed an increase in T_g to 267 °C. This temperature is close to the T_g's of cured samples of oligomers **22** and **23**; we believe this demonstrates that effective cross-linking had taken place, even though an exact value for the precure T_g of **24** could not be obtained. Again, the ring-opening exotherm had completely disappeared, indicating complete thermal curing of the end groups.[16]

Oligomer Processing and Cured Properties. Samples of the BCB end-capped oligomer **22** were melt-processed at 350 °C for varying times and under various pressures. Samples simply melt-pressed between the heated platens showed almost no flow and poor consolidation, even at higher temperatures and pressures than those used to effectively cure cyclophane-capped oligomers **25**.[2] These samples also turned brown, appearing to have undergone some thermooxidative degradation. Subsequent samples were prepressed in a 0.5-in.-diameter KBr pellet press under 24 000 lb and showed fairly good consolidation after heating between the heated platens under 25 000 lb to complete the cure. The resulting yellow films were of poor quality, however, and were opaque and quite heterogeneous. It was thought that the low ring-opening temperature of benzocyclobutene (277 °C) afforded rapid curing, resulting in rigidification of the samples before good flow had taken place. However, samples that were cured at lower temperatures (250–270 °C) under the same pressure showed no improvement in quality. In fact, an improved film was produced by curing

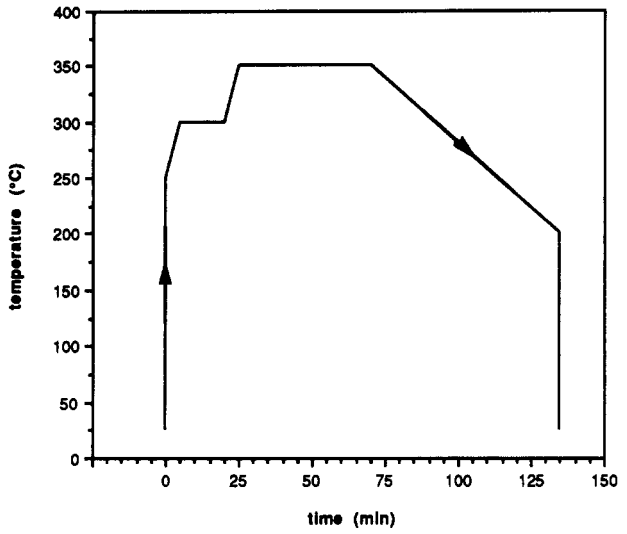


Figure 6. Temperature cycle for curing of best films.

at 300–350 °C under 25 000 lb for 3 h. This film exhibited the best flow and was homogeneous, transparent, and yellow. The cured samples exhibited T_g's of 263 °C or higher, an increase of 32 °C over that of the uncured powder sample.

Several powder samples of CBQ-capped oligomer **23** were also melt-processed under various conditions of temperature and pressure. A sample that was melt-pressed directly between the heated platens (without preconsolidation) showed better flow than had oligomer **22**, but excessive decomposition was observed throughout most of the sample, leading us again to preconsolidate the subsequent samples at room temperature in a KBr press before high-temperature processing. The resulting films were of poor quality and were again opaque and heterogeneous, although much less oxidative decomposition was evident. An improved film was again obtained by curing under more stringent conditions (3 h at 300–350 °C under 25 000 lb); this film exhibited some flow and was transparent and orange. The completely cured samples of CBQ-capped **23** exhibited T_g's of 265 °C or higher, an increase of 44 °C over that of the uncured powder sample, and were insoluble after 24 h in refluxing *sym*-tetrachloroethane.

A sample of the BCBAN end-capped oligomer **24** was melt-processed under the same conditions and again gave a transparent, yellow film. The cured sample exhibited a T_g of 267 °C and was insoluble after 24 h in refluxing *sym*-tetrachloroethane.

Another film sample from **24**, pressed at only 300 °C, was of poor quality, even though a cure temperature of 300 °C should have been adequate to result in complete curing of the end groups. Film quality thus seemed to be more dependent on melt flow during processing than on the rate of cross-linking, although these factors are clearly interrelated.

Several samples of a previously prepared[2] DP = 22 [2.2]-paracyclophane end-capped oligomer **25** were preconsolidated in a KBr press and melt-pressed under various conditions of temperature, pressure, and time. It was found that good quality, transparent, homogeneous films could be obtained by pressing each sample disk between two 1-in.-diameter copper disks under a load of 31 416 lb (40 000 psi). The optimized temperature cycle is shown in Figure 6. The initial platen temperature was 250 °C. After the sample was placed under pressure, the temperature was raised to 300 °C. After 15 min at this temperature, the temperature was again increased to 350 °C and this temperature was maintained for 45 min. Finally, the sample was allowed to cool to ~200 °C and quenched as usual (see Experimental Section).

These cure conditions were used to process samples of each of the oligomers, giving in every case high-quality transparent films that exhibited good flow. During processing, the sample disks expanded to about 1.5–2 times their original areas (70-mg sample disks).

Differential scanning calorimetry and dynamic mechanical analysis (DMA) were carried out on the best cured films (Table III). The films showed no solubility after 24 h in refluxing *sym*-tetrachloroethane (TCE). A film from the analogous phenyl end-capped oligomer[18] was melt-pressed for 2 h at 300 °C and 1 h at 350 °C for comparison; the resulting transparent, yellow film containing inert phenyl end groups was completely soluble in refluxing *sym*-tetrachloroethane, demonstrating that no significant thermal cross-linking occurs, under these cure conditions, in the absence of reactive end groups.

The T_g's for the best cured films occurred at somewhat lower temperatures than those of poorer quality films from the same oligomers. Since none of the film samples exhibited ring-opening exotherms by DSC, and all were insoluble, there is no reason to suppose that the lower T_g's represent incomplete cross-linking.

Dynamic mechanical analysis (Table III) indicated that the flexural storage moduli (E') of the cured films were fully consistent with values obtained for previous films from cured polyquinoline oligomers.[2,19] The maxima of the flexural loss moduli (E''_{max}) occurred 42–55 °C higher than the corresponding T_g's from DSC. The maximum tan δ occurred 6–8 °C above the E''_{max} for each of the film samples. A comparison of the post-T_g storage moduli (E') of the films shows that the new end caps (CBQ and BCBAN) are effective cross-linkers, giving films with cross-link densities at least as high as that of the film cross-linked with BCB end groups.

The short-term thermal stability of the cured films was examined by thermogravimetric analysis (TGA). All films exhibited good thermal stability to ~550 °C (onset) in argon and 535 °C in air, with the maximum rate of weight loss ("break") occurring at about 575 °C in argon and 560 °C in air. Samples analyzed under argon exhibited 68–78% weight remaining after analysis up to 900 °C.[20] The onsets of weight loss in air were significantly lower for the poorer quality films from BCB-capped oligomer **22**, but increased to acceptable values in the better quality film samples.

Thermogravimetric analysis only provides information on short-term thermal properties and thus shows little variation with end-cap identity unless very large differences in stability are present. Short-term weight loss characteristics are also often more dependent on sample quality and geometry than on inherent chemical stability; reasonable-quality films from all the studied oligomers showed good thermooxidative stability by TGA.

Isothermal aging experiments carried out on samples of the oligomers in a circulating air oven at 320 °C gave data that were somewhat ambiguous, presumably as a result of the difficulty of controlling various experimental variables such as the sample geometry and uniformity of temperature and air flow throughout the oven, as well as the difficulty of collecting data at enough aging times to be sure of the accuracy of the observed weight loss trends.

In order to obtain a better comparison of the best film samples, we turned to isothermal gravimetric analysis (IGA), using the same instrumentation that was used to obtain TGA data. This method allowed a continuum of

Table III
Thermal and Mechanical Properties[a] of Best Cured Films[b] from End-Capped Oligomers

oligomer	end cap	T_g, °C	E''_{max}, °C	$(\tan \delta)_{max}$	$E'_{50°C}$, GPa	$E'_{345°C}$, MPa
22	BCB	245	287	295	1.95	9.00
23	CBQ	258	301	309	3.53	15.3
24	BCBAN	257	303	311	2.68	17.7
25[c]	PCP	253	308	314	1.92	17.4

[a] T_g's are from DSC, other properties are from DMA. [b] Cured under a load of 31 416 lb (ca. 40 000 psi) in air following the temperature cycle of Figure 6. [c] Prepared in previous work.[2]

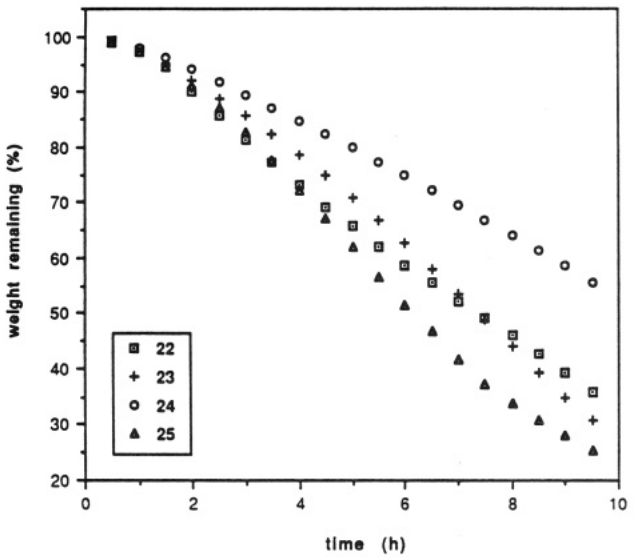


Figure 7. Isothermal gravimetric analysis of best cured films at 400 °C.

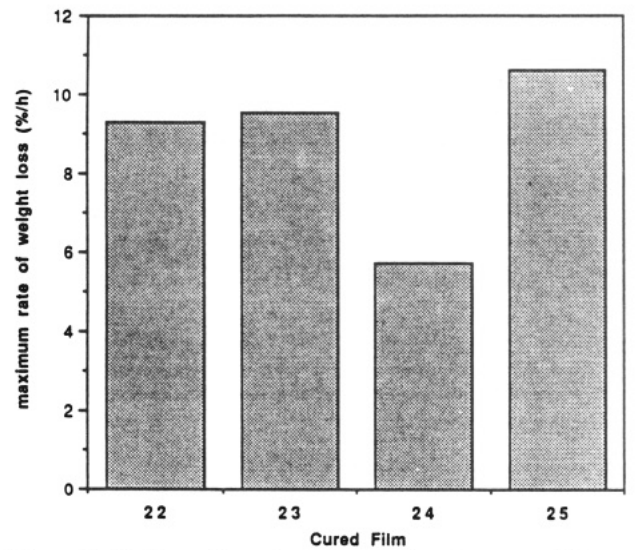


Figure 8. Isothermal gravimetric analysis of best cured films at 400 °C.

data to be collected under closely controlled conditions. There is still some possibility that sample weight and geometry may affect the rate of weight loss, but this method is a significant improvement over the previously used isothermal aging method. In addition to a continuum of weight/time data, a maximum rate of weight loss can also be determined from the first derivative curve, providing another index of thermooxidative stability.

Isothermal gravimetric analysis was carried out on the best films at 400 °C in air over the course of 17 h. The results are shown in Figures 7 and 8. The new BCBAN end-capped oligomer **24** gave a film clearly superior to that from the analogous BCB end-capped oligomer **22** (Figure 7). However, some of this superior stability may result from the apparently higher molecular weight of BCBAN-capped oligomer **24**, relative to BCB- and CBQ-capped oligomers **22** and **23** (based on viscosity measurements), and hence the lower end-group density in **24**. The new CBQ end cap gave stability comparable to that of BCB.

The maximum rate of weight loss (Figure 8) is lowest for the cured film from oligomer **24**. This indicates that weight loss occurred less catastrophically for this film than for films from the other oligomers. The BCB- and CBQ-derived films were again comparable. The maximum rates of weight loss are consistent with the trend exhibited in the full IGA trace (Figure 7).

Conclusions

Three acetylated ring systems were synthesized and incorporated into quinoline oligomers as reactive end groups. The oligomers were characterized, and cure conditions were optimized to give good quality, transparent films. Isothermal gravimetric analysis was a more satisfactory method for comparing the long-term thermooxidative stability of film samples than was the isothermal aging method used previously.

All of the studied ring systems gave more convenient thermal cure temperatures than the previously studied[1,19] biphenylene system, rendering the use of metal ring-opening catalysts unnecessary.

The benzocyclobutene ring system gave an oligomer (**22**) with poor melt-flow properties, compared to the analogous [2.2]paracyclophane end-capped oligomer **25**.[2] Increasing the cure pressure did provide a good-quality cured film that showed mechanical properties comparable to films from cyclophane- and biphenylene-capped oligomers. The thermooxidative stability of films from **22** was significantly greater than that of the analogous cyclophane-capped oligomer **25**.

The novel end caps 6-acetyl-8-phenyl-1,2-dihydro[3,4]-cyclobuta[1,2-*b*]quinoline (CBQ) (**11**) and 8-acetyl-6b,-10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (BCBAN) (**19**) gave quinoline oligomers (**23** and **24**) with melt-flow properties similar to those of BCB-capped oligomer **22**. The optimal cure conditions afforded good-quality, transparent films with good thermal and mechanical properties. The thermooxidative stability of the best film from the CBQ-capped oligomer was similar to that of films from BCB-capped oligomer **22**, by IGA. The BCBAN end-capped oligomer **24** afforded a film with significantly better thermooxidative stability than that of films from BCB-capped oligomer **22** and CBQ-capped oligomer **23**, by IGA.

Hence, the readily synthesized CBQ and BCBAN end caps show promise as new reactive cross-linkers to replace the benzocyclobutene system, and this advantage should hold true in other cure resin systems where the BCB end cap has been, and continues to be, utilized. This is particularly true in the case of the BCBAN ring system, which opens thermally at 234 °C, a temperature that should be convenient for lower T_g cure resins.

Experimental Section

The monomers 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**20**)[14a] and 4,4′-diacetyldiphenyl ether (**21**)[14b] and the catalyst di-*m*-cresyl phosphate[21] were prepared and purified according to the published procedures, as were (1-ethoxyvinyl)trimethylstannane,[8b] and tetrakis(triphenylphosphine)palladium(0).[22]

All melting points are uncorrected and were determined by use of a Mel-Temp apparatus. Elemental analyses were carried out by Atlantic Microlab, Inc. of Norcross, GA.

A Bruker AC300P NMR spectrometer was used to record 300-MHz proton (^{1}H) spectra, and 75.5-MHz carbon (^{13}C) spectra. Proton chemical shifts are reported in ppm (δ) downfield from internal tetramethylsilane and carbon chemical shifts are reported in ppm (δ) downfield relative to deuteriochloroform (δ = 77 ppm).

Intrinsic viscosity measurements on polymer solutions in chloroform were carried out with a No. 50 Cannon-Ubbelohde microdilution viscometer. The chloroform was HPLC grade and was passed through alumina to remove the ethanol inhibitor. Viscosity measurements were taken at 25.00 ± 0.05 °C on polymer solutions with concentrations of 0.500, 0.400, 0.333, and 0.250 g/dL. The reduced (η_{red}) and inherent (η_{inh}) viscosities were calculated and graphed vs concentration. The average of the y intercepts of the two lines was taken as the value for intrinsic viscosity [η].

Thermal and mechanical analyses of the oligomers and melt-pressed films were carried out using a Du Pont 9900 thermal analyzer with a Du Pont 910 differential scanning calorimeter (heating rate 20 °C/min), a Du Pont 951 thermogravimetric analyzer (heating rate 10 °C/min), and a Du Pont 983 dynamic mechanical analyzer (heating rate 5 °C/min, horizontal clamps, resonant mode). Uncured powder samples were prepared for DSC and TGA analysis by pressing 70-mg samples of the polymer in a KBr pellet die for 10 min under a 24 000-lb load in a Carver laboratory press, Model 1726. Isothermal aging studies were carried out on 25–70-mg film samples, which were placed in weighed vials, covered with watch glasses, and allowed to age in a 320 °C gas chromatograph oven in an atmosphere of circulating air.

m-Cresol was distilled under nitrogen just prior to use. Tetrahydrofuran, ethyl ether, and 1,2-dichloroethane for use in benzyne reactions were dried over magnesium sulfate and filtered.

Flash chromatography was carried out using 32–63-μm silica gel. Hexanes and ethyl acetate were distilled prior to use as chromatography solvents; other solvents were used as obtained (reagent grade). Preparative thin-layer chromatography (PTLC) was carried out on 20 × 20 cm glass plates coated with 2 mm thick 60 F_{254} Kieselgel (Merck No. 5717, purchased from EM Science).

4-Acetylbenzocyclobutene (5). Into a 100-mL flask equipped with a stir bar and containing 1.516 g (8.282 mmol) of 3- and 4-bromobenzocyclobutenes (**4**) were charged 1.766 g (7.518 mmol) of (1-ethoxyvinyl)trimethylstannane and 20 mL of degassed toluene (freshly distilled from sodium). The mixture was sparged with nitrogen for 10 min, and 249 mg (0.215 mmol) of tetrakis-(triphenylphosphine)palladium(0) (triturated with warm, degassed ethanol and dried) was added in one portion. The mixture was sparged with nitrogen for 10 min more and then stirred and heated at reflux in the dark for 48 h under static nitrogen. The reaction mixture was allowed to cool to room temperature, diluted to 50 mL with *n*-pentane, and partitioned between pentane and water. The aqueous layer was extracted three times with fresh pentane, and the combined organic layers were washed twice with 10% aqueous ammonia, twice with water, and once with saturated aqueous NaCl and dried over $MgSO_4$. The organics were filtered and the solvent was removed under reduced pressure to give a yellow oil. The crude intermediate oil was dissolved in 20 mL of tetrahydrofuran (THF) and 4 mL of water was added to the solution, followed by 4 mL of 1 N HCl. The mixture was stirred at room temperature for 3 days in the dark and then partitioned between pentane and water. The aqueous phase was extracted three times with fresh pentane and once with ethyl ether, and the organics were combined, washed twice with water and once with saturated aqueous NaCl, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure to give a yellow oil. The oil was purified by preparative TLC on 2-mm silica plates, eluting with 2:1 hexanes/ethyl acetate. The product band was isolated and extracted with ethyl ether. The solvent was removed under reduced pressure to give 0.583 g (48%) of an off-white solid, which consisted of both the 3- and 4-acetylbenzocyclobutenes by ^{1}H NMR. Recrystallization was carried out in *n*-pentane at −60 °C under an atmosphere of nitrogen. The supernatant was removed by syringe, and the solid material was redissolved and recrystallized again 10 more times to yield 0.128 g (11%) of off-white crystalline 4-acetylbenzocyclobutene (**5**). The supernatants were reduced and a second crop was taken to give, after eight recrystallizations, 0.133 g of light tan crystals (combined yield 21%): mp 35.4–36.4 °C uncorr (lit.[6] mp 34–35 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, 1), 7.65 (s, 1), 7.13 (d, 1), 3.21 (s, 4), 2.57 (s, 3); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 198.3, 152.0, 146.0, 136.3, 127.7, 122.4, 122.3, 29.84, 29.35, 26.63. Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89; O, 10.94. Found: C, 81.95; H, 6.94; O, 11.06.

6-Bromo-8-phenyl-1,2-dihydro[3,4]cyclobuta[1,2-*b*]quinoline (10). The conditions for a similar reaction were reported in the literature.[9a,b] Into a 1-L flask containing a stir bar and a solution of 80 g (1.43 mol) of potassium hydroxide in 525 mL of ethanol were charged 17.03 g (61.67 mmol) of 2-amino-5-bromobenzophenone (**9**)[10] and 5 g (71 mmol) of cyclobutanone (**7**). The yellow solution was stirred for 5 days under an atmosphere of static nitrogen and then warmed at 50 °C for 24 h. The mixture was allowed to cool, reduced by rotary evaporation, and partitioned between chloroform and water. The aqueous phase was extracted three times with fresh chloroform, and the organics were combined, washed once with water and twice with saturated aqueous NaCl, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure to give a yellow oil, which solidified upon standing. Proton NMR analysis showed a ratio of starting **9** to product **10** of ~2:1. The yellow solid was redissolved in chloroform and dry-packed on silica. Flash chromatography on silica (500-mL dry volume), eluting with 2:1 hexanes/ethyl acetate, gave three major overlapping bands and two smaller, low-R_f bands. The two highest R_f, yellow, major bands were combined; the first yellow band represented recovered starting **9**, and the identity of the second compound was not determined. The third, less colored band contained mostly desired product **10**. The low-R_f bands were discarded. The eluent containing the product band was reduced by rotary evaporation and rechromatographed twice more, as before, to remove more of the **9** and side products. The solvents were removed under reduced pressure to give 4.366 g (23%) of a viscous yellow oil, which crystallized upon standing. This material was carried on in the next step (vide infra).

A smaller batch of **10**, prepared similarly, was fully purified as follows: After the aqueous workup, the mixture was recrystallized twice from 95% ethanol to remove the large portion of starting **9**. The yellow crystals were suction-filtered and the filtrates were combined and reduced by rotary evaporation. A portion of the yellow oil was purified by preparative TLC on a 2-mm silica plate, eluting with 2:1 hexanes/ethyl acetate. Two major bands were obtained. The R_f = 0.57 band was bright yellow and consisted of starting **9**. The light yellow R_f = 0.31 band consisted of pure product **10**. The large portion of the yellow oil was purified by flash chromatography on silica, eluting with 2:1 hexanes/ethyl acetate, and gave good separation. The product band was combined with that from the previous PTLC separation and the solvents were removed under reduced pressure. The light yellow oil was rechromatographed by flash chromatography as before, and the product-containing fractions were combined. The solvents were removed under reduced pressure to give a light yellow oil that crystallized upon standing. The solid **10** was recrystallized once from hexanes and three times from *n*-pentane to give light tan crystals: mp 106.7–107.5 °C uncorr; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (s, 1), 7.96 (d, 1), 7.69 (dd, 1), 7.51 (m, 5), 3.56 (dd, 2), 3.24 (dd, 2); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 166.2, 148.5, 138.9, 137.6, 133.9, 131.2, 131.0, 129.4, 129.1, 128.9, 128.7, 127.9, 119.2, 34.7, 26.2. Anal. Calcd for $C_{17}H_{12}BrN$: C, 65.83; H, 3.90; Br, 25.76; N, 4.52. Found: C, 65.82; H, 3.90; Br, 25.70; N, 4.50.

Differential scanning calorimetry was carried out on a sample of pure **10** from 50 to 400 °C under argon, at a heating rate of 20 °C/min. The melting endotherm appeared at 112 °C, and the maximum of the ring-opening exotherm occurred at 336 °C.

Integration of the area under the exotherm gave a value of 61.26 cal/g, which corresponds to 19.00 kcal/mol of energy released during ring opening. The sample appeared to be stable to ~370 °C.

6-Acetyl-8-phenyl-1,2-dihydro[3,4]cyclobuta[1,2-*b*]quinoline (11). The ethoxyvinylation and hydrolysis of 6-bromo-8-phenyl-1,2-dihydro[3,4]cyclobuta[1,2-*b*]quinoline (**10**) was carried out as for the synthesis of 4-acetylbenzocyclobutene (**5**) (vide supra), using 1.940 g (6.254 mmol) of **10**, 1.357 g (5.777 mmol) of (1-ethoxyvinyl)trimethyltin, 194 mg (0.168 mmol) of tetrakis(triphenylphosphine)palladium(0), and 42 mL of degassed toluene. For the hydrolysis, 20 mL of THF, 4 mL of 10% aqueous HCl, and 4 mL of water were used. The same aqueous workup was carried out, with the addition that the aqueous phase was also extracted with chloroform. The ether/pentane organics were kept separate from the chloroform organics during the workup and drying. The organics were combined and filtered, and the solvents were removed under reduced pressure. The dark material was purified by preparative TLC on 2-mm silica plates, eluting with 1:1 benzene/ethyl acetate. The product band was isolated and extracted with ethyl ether and chloroform, and the solvents were removed under reduced pressure to give 0.877 g (56%) of yellow solid **11**. The material was rechromatographed as before and then recrystallized twice from ether/pentane to give 223 mg (14%) of light yellow flakes. A second crop brought the combined yield to 27%: mp 159.7–160.5 °C uncorr; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62 (s, 1), 8.18 (d, 1), 8.15 (d, 1), 7.55 (m, 5), 3.62 (dd, 2), 3.30 (dd, 2), 2.61 (s, 3). Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.12; O, 5.85. Found: C, 83.54; H, 5.53; N, 5.09; O, 5.82.

Differential scanning calorimetry was carried out on a sample of pure **11** from 50 to 600 °C under argon, at a heating rate of 20 °C/min. The melting endotherm appeared at 164 °C, and the maximum of the ring-opening exotherm occurred at 352 °C. Integration of the area under the exotherm gave a value of 76.32 cal/g, which corresponds to 20.86 kcal/mol of energy released during ring opening. The sample appeared to be stable up to ~450 °C.

4-Bromobenzenediazonium-2-carboxylate. Following a procedure reported for the synthesis of the parent benzenediazonium-2-carboxylate,[23] 2.205 g (10.21 mmol) of 5-bromoanthranilic acid, 0.0257 g (0.1573 mmol) of trichloroacetic acid, 40 mL of tetrahydrofuran, and a stir bar were placed in a flame-dried 50-mL flask. The mixture was cooled in an ice–water bath under nitrogen, and 1.6 mL (1.4 g, 12 mmol) of isoamyl nitrite was added dropwise with stirring. After 2 h, the mixture was allowed to warm to room temperature and stirred for 3 h. The mixture initially turned dark red-orange, and later the red coloration disappeared and a tan precipitate formed. The mixture was cooled in an ice–water bath and suction filtered (making sure that the precipitate never became dry; *dry benzenediazonium-2-carboxylates can detonate violently*!), rinsing with cold THF and cold ethyl ether. The tan solid, 4-bromobenzenediazonium-2-carboxylate, was then carried on in the next step (vide infra), under the assumption that it had been obtained in roughly quantitative yield. Any remaining, unused residues of the tan product were immediately diluted in water and washed away.

8-Bromo-6b,10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (18). To a 500-mL flask containing 80 mmol of 4-bromobenzenediazonium-2-carboxylate (vide supra), 200 mL of 1,2-dichloroethane, and a stir bar was added 24.367 g (160.10 mmol) of acenaphthylene (Lancaster Synthesis, used as obtained). The mixture was heated for 24-h periods at room temperature, 41 °C, and 42 °C. The mixture was then gradually heated to 58 °C over 10 h, whereupon it became dark and homogeneous. The mixture was allowed to cool and the solvent was removed under reduced pressure. The dark, viscous liquid was partitioned between benzene/chloroform and water and the aqueous layer was extracted three times each with benzene and chloroform. The dark organics were combined, washed once with saturated aqueous $NaHCO_3$, twice with water, and twice with saturated NaCl, dried over $MgSO_4$, and filtered. The solvents were removed under reduced pressure to give a dark brown oil. Thin-layer chromatography, eluting with *n*-pentane, indicated that the yellow, starting acenaphthylene forms the major component at $R_f = 0.35$, and the smaller, colorless band at $R_f = 0.20$ was assumed to be the desired product. The dark oil was dry-packed on silica (250-mL dry volume) and flash chromatography on silica, eluting with *n*-pentane, allowed fair separation of the starting acenaphthylene from the colorless product **18**. The solvent was removed from the product fraction under reduced pressure to give a white solid. Trituration with pentane followed by two recrystallizations from cyclohexane/pentane and two recrystallizations from pentane gave in three crops 4.124 g (17%) of white, microcrystalline **18**: mp 134.5–135.3 °C uncorr; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (m, 2), 7.46 (m, 4), 7.32 (s, 1), 7.25 (t, 1), 7.04 (d, 1), 5.33 (d, 1), 5.28 (d, 1); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 148.5, 145.6, 142.1, 141.9, 138.8, 132.5, 130.7, 127.9, 127.1, 125.9, 124.2, 124.0, 123.9, 121.2, 119.9, 119.8, 53.8, 53.6. Anal. Calcd for $C_{18}H_{11}Br$: C, 70.38; H, 3.61; Br, 26.01. Found: 70.33; H, 3.60; Br, 25.92.

Differential scanning calorimetry was carried out on a sample of pure **18** from 50 to 500 °C under argon, at a heating rate of 20 °C/min. The melting endotherm appeared at 141 °C, and the maximum of the ring-opening exotherm occurred at 234 °C. Integration of the area under the exotherm gave a value of 82.45 cal/g, which corresponds to 25.32 kcal/mol of energy released during ring opening. Several other exothermic peaks were observed, the largest appearing at 361, 456, and 485 °C.

8-Acetyl-6b,10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (19). The ethoxyvinylation and hydrolysis of 8-bromo-6b,10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (**18**) was carried out as for the synthesis of compound **5**, using 2.948 g (9.597 mmol) of **18**, 2.255 g (9.600 mmol) of (1-ethoxyvinyl)trimethyltin, 300 mg (0.260 mmol) of tetrakis(triphenylphosphine)palladium(0), and 50 mL of degassed toluene. For the hydrolysis, 30 mL of THF, 6 mL of 10% aqueous HCl, and 6 mL of water were used. The crude ethoxyvinyl intermediate was characterized: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (dd, 2), 7.49–7.40 (m, 5), 7.21–7.12 (m, 2), 5.33 (s, 2), 4.46 (d, 1), 4.07 (d, 1), 3.62 (q, 2), 1.36 (t, 3).

The same aqueous workup was carried out, with the addition that the aqueous phase was also extracted with chloroform. The ether/pentane organics were kept separate from the chloroform organics during the workup and drying. The organics were combined and filtered, and the solvents were removed under reduced pressure. The off-white solid was purified by flash chromatography on silica (500-mL dry volume), eluting with chloroform. The solvents were removed under reduced pressure to give 2.023 g (78%) of white solid **19**. Recrystallization from chloroform/hexanes afforded 1.774 g (68%) of white crystals in two crops: mp 162.8–163.4 °C uncorr; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (m, 2), 7.63 (d, 2), 7.54–7.45 (m, 4), 7.24 (d, 1), 5.39 (s, 2), 2.50 (s, 3); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 197.9, 152.7, 147.4, 142.0, 141.7, 138.8, 136.9, 132.4, 128.6, 128.3, 127.93, 127.90, 124.0, 123.9, 122.4, 122.3, 119.9, 54.1, 53.7, 26.6. Anal. Calcd for $C_{20}H_{14}O$: C, 88.86; H, 5.22; O, 5.92. Found: C, 88.69; H, 5.25; O, 5.99.

Differential scanning calorimetry was carried out on a sample of pure **19** from 50 to 500 °C under argon, at a heating rate of 20 °C/min. The melting endotherm appeared at 161 °C, and the maximum of the ring-opening exotherm occurred at 237 °C. Integration of the area under the exotherm gave a value of 134.2 cal/g, which corresponds to 36.28 kcal/mol of energy released during ring opening.

Benzocyclobutene End-Capped Polyquinoline (DP = 22) (22). Following the procedure reported for the synthesis of end-capped polyquinoline oligomers,[1] 1.316 854 g (3.223 983 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**20**), 0.763 116 g (3.001 03 mmol) of 4,4′-diacetyldiphenyl ether (**21**), 22.515 g of di-*m*-cresyl phosphate, and 3.803 g of distilled *m*-cresol were charged to a three-necked resin kettle equipped with a nitrogen inlet, a mechanical stirrer, and a nitrogen outlet. The flask was flushed with nitrogen for ~10 min with stirring and then was placed in an oil bath heated to 138 °C. Stirring was continued for 28 h under static nitrogen. Stirring and heating were halted while a solution of 0.230 g (1.56 mmol) of 4-acetylbenzocyclobutene (**5**) in 0.720 g of *m*-cresol was added to the mixture. The flask was rinsed with 0.914 g of *m*-cresol, which was also added to the polymerization pot. Stirring and heating were continued for 12 h at 110 °C and then for 4.5 h at 135 °C. The viscous, hot reaction mixture was poured slowly into a stirred solution of 450 mL of ethanol and 50 mL of triethylamine. The

resulting mixture was stirred for 1 h, chopped in a Waring blender (on low setting for 30 s and then on high for 45 s), and filtered. The solid polymer was continuously extracted for 19 h with ethanol containing 10% (v/v) triethylamine, air-dried, and then dried at 110 °C under reduced pressure for 8 h. The polymer was redissolved in 90 mL of chloroform and reprecipitated by slow addition, through a plug of glass wool, to a stirred solution of 900 mL of ethanol and 100 mL of triethylamine (both filtered through a glass frit). The polymer **22** was collected by filtration and dried as before, giving 1.7 g (85%) of a fine, white powder: intrinsic viscosity $[\eta]$ = 0.526 ($CHCl_3$, 24.97 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 3.26 (s, end-cap CH_2). Anal. Calcd: C, 85.50; H, 4.46; N, 4.73. Found: C, 84.76; H, 4.51; N, 4.67.

Cyclobuta[*b*]quinoline End-Capped Polyquinoline (DP = 22) (23). Into the bottom of a resin kettle equipped with a nitrogen inlet, a mechanical stirrer, and a nitrogen outlet were charged 1.3175 g (3.2256 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**20**), 0.7635 g (3.0025 mmol) of 4,4′-diacetyldiphenyl ether (**21**), 22.580 g of di-*m*-cresyl phosphate, and 3.803 g of distilled *m*-cresol. The procedure and workup were the same as that used for **22**, using 0.353 g (1.29 mmol) of 6-acetyl-8-phenyl-1,2-dihydro[3,4]cyclobuta[1,2-*b*]quinoline (**11**) to end-cap the oligomer. Fresh *m*-cresol (2 mL) was used to rinse the end cap into the polymerization vessel. Stirring and heating were continued for 24 h at 122 °C and then for 30 min at 135 °C. A fine, light tan powder (1.90 g, 89%) was obtained: intrinsic viscosity $[\eta]$ = 0.463 ($CHCl_3$, 25.00 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 3.63 (m, 2, end-cap CH_2), 3.30 (m, 2, end-cap CH_2). Anal. Calcd: C, 85.51; H, 4.46; N, 4.85. Found: C, 83.58; H, 4.49; N, 4.72.

Benzo[*j*]cyclobut[*a*]acenaphthylene End-Capped Polyquinoline (DP = 22) (24). Into the bottom of a resin kettle equipped with a nitrogen inlet, a mechanical stirrer, and a nitrogen outlet were charged 1.3161 g (3.2221 mmol) of 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (**20**), 0.7627 g (2.9994 mmol) of 4,4′-diacetyldiphenyl ether (**21**), 22.535 g of di-*m*-cresyl phosphate, and 3.808 g of distilled *m*-cresol. The procedure and workup were the same as that for **22**, using 0.270 g (0.999 mmol) of 8-acetyl-6b,10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (**19**) to end-cap the oligomer. Fresh *m*-cresol (1 mL) was used to rinse the end cap into the polymerization vessel. Stirring and heating were continued for 12 h at 120 °C, 12 h at 110 °C, and then 30 min at 135 °C. An off-white powder (1.74 g, 84%) was obtained: intrinsic viscosity $[\eta]$ = 0.813 ($CHCl_3$, 24.93 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 5.45 (br s, end-cap CH). Anal. Calcd: C, 85.55; H, 4.44; N, 4.70. Found: C, 84.85; H, 4.48; N, 4.73.

Neat Resin Melt Processing. A Wabash hydraulic press (Model 1210) that had been fitted with Carver heat platens was used for melt processing. The platens were heated to the desired cure temperature while the polymer sample was prepared. In the early samples, a 200-mg powder sample of the polymer was placed in a small pile between two copper sheets (0.10 in. thick). Two L-shaped pieces of copper sheet were used as spacers surrounding the sample. The assembly was placed between the preheated platens and melt-processed at 350 °C under a 5000-lb load for the desired amount of time. The platens were allowed to cool to 200 °C without releasing the pressure, whereupon the sample assembly was removed from the press and quickly plunged into tap water. The copper sheets were carefully peeled away from the cured film, which was swirled in concentrated aqueous ammonia for 30 min, thoroughly rinsed with water, and air-dried. Later samples were consolidated in a 0.5-in.-diameter KBr press under 24 000 lb for 30 min before melt-pressing at elevated temperatures. The best samples were cured without copper spacers, between two 1-in.-diameter copper disks under the temperature conditions shown in Figure 6. The films were quenched, washed, and dried as before.

Acknowledgment. This research was made possible by a grant from the Army Research Office, Research Triangle, NC, whose support we gratefully acknowledge. We also thank Alex J. Parker for GPC work.

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(12) Bromobenzyne was generated by the thermal decomposition of 4-bromobenzenediazonium-2-carboxylate (Experimental Section).
(13) In our work, 4-bromobenzenediazonium-2-carboxylate was allowed to decompose slowly at a mild temperature in the presence of an excess of acenaphthylene (**13**) (Experimental Section). The previous workers[11a] had used a different technique for producing benzyne, where a solution of anthranilic acid was added slowly to a refluxing solution containing isoamyl nitrite and **13**, forming the benzyne in situ.
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(16) The cure effectiveness was also demonstrated by the insolubility of the cured polymer films (vide infra).
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