those of the poly(ether–imide) analogue, consistent with the expected affect of pendent phenyl groups.[15] In addition, **6a** showed a decomposition temperature of 520 °C (5 °C/min heating rate, nitrogen atmosphere), comparable to **1** (PDT = 540 °C).[16] Isothermal aging of **6a** at 400 °C (nitrogen atmosphere) resulted in a weight loss rate of 0.05 wt %/h, slightly higher than that of **1** (0.02 wt %/h), yet comparable to that of PMDA-ODA polyimide (0.04 wt %/h). Thus, these materials represent a class of high-T_g thermoplastics with excellent thermal stability.

The results demonstrate that quinoxaline-based poly(aryl ethers) can be synthesized via a halo displacement polymerization, where the fused pyrazine ring is the activating group. The polymerization provides a general method for the preparation of aryl ether based PPQs, where the structure of the aryl ether moiety is readily controlled by varying the bisphenol used. The materials obtained by this method are the PPQ analogue of the poly(ether–imides) and should show many of the same desirable properties including good melt and solution processability. Moreover, heterocyclic activated nucleophilic displacement chemistry should prove effective with monomers derived from other ring systems, providing a general synthetic methodology to high-temperature, high-T_g aryl ether–heterocyclic polymers.

Future work on poly(aryl ether–phenylquinoxalines) will focus on demonstrating the scope of materials possible by utilizing bisquinoxaline monomers derived from other bis(α-diketones) as well as other bisphenols. Further studies on the polymerization process will entail leaving group effects (i.e., chloro, nitro), ether interchange, and molecular weight control. In addition, the mechanical and thermal properties will be investigated together with both the solution and melt viscosities.

Registry No. **2**, 114583-79-8; **3**, 114583-80-1; **4**, 114583-85-6; **6a** (copolymer), 114583-86-7; **6a** (SRU), 114633-53-3; **6b** (copolymer), 114613-38-6; **6b** (SRU), 114633-54-4; **6c** (copolymer), 114613-39-7; **6c** (SRU), 114633-55-5; sodium *m*-cresolate, 3019-89-4; 1,1-bis(phenyl glyoxalyl)benzene, 3363-97-1; 4-fluoro-1,2-phenylenediamine, 367-31-7.

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Preparation of Polyacetylene Chains in Low-Polydispersity Diblock and Triblock Copolymers

Studies of polyacetylene have been hampered by its intractability and (especially when doped) its sensitivity to air.[1] It would be desirable to prepare well-defined solubilized polyacetylene samples in order to more fully understand interchain and intrachain phenomena (especially those relevant to electrical conduction) and polymer morphology. Many grafts,[2] blends,[3] and blocks[4] containing polyacetylene have been made by classical techniques, and considerable control over polymer purity and morphology is now possible through the Feast (ring opening) method of preparing polyacetylene.[5] However, there is still a need for absolute control over polymer preparation, ideally to give soluble, block copolymers with as narrow a molecular weight distribution as is possible.[6] We report such a method here.

Tungsten[7a] or molybdenum[7b] catalysts of the type M(CHR)(NAr)$(OCMe_3)_2$ (R = alkyl or polymer chain; Ar = 2,6-C_6H_3-*i*-Pr_2) have been shown to polymerize norbornene to give essentially monodisperse polynorbene and (when M = Mo) poly-*endo*-5,6-dicarbomethoxynorbornene, as well as block copolymers.[8] 7,8-Bis(trifluoromethyl)tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (**1**; Scheme I) is also smoothly polymerized by these catalysts.[9,10] Similarly, block copolymers ($\mathbf{3}^{A-B}$ and $\mathbf{3}^{A-B-A}$ in Scheme I) can be synthesized by the sequential addition of **1** and norbornene (**2**) to Mo$(CHCMe_3)$(NAr)$(OCMe_3)_2$[11] followed by cleavage with benzaldehyde or pivaldehyde. The order of addition of **1** or **2** can be reversed with similar results. GPC analyses of representative polymers are shown in Table I.

Upon heating **3**,[12] *o*-$C_6H_4(CF_3)_2$ is eliminated to generate a polyene chain containing $2B + 1$ double bonds attached to one polynorbornene chain ($\mathbf{4}^{A-B}$) or two polynorbornene chains ($\mathbf{4}^{A-B-A}$) (Scheme I). The results of GPC studies (in dichloromethane) on these orange to deep red, toluene-soluble, block copolymers **4** are analogous; those for $\mathbf{4}^{A-B-A}$ are listed in Table II. When $B = 5$ the polymer has a molecular weight and low polydispersity characteristic of a well-behaved system. When $B = 10$, 15, or 20, a new, relatively high molecular peak is observed that dominates when $B = 20$ (an average of 41 double bonds). We hypothesize that the high molecular weight fraction results from aggregation or cross-linking of the polyene chains in the expected macromolecule. Note that the number of macromolecules that make up the "aggregate" (N = high M_n/low M_n) increases with B; for $A = 100$, $N = 8.4$, 10.0, and 12.6 for $B = 10$, 15, and 20, respectively. Also note the N decreases as A increases; for $B = 15$, $N = 13.4$ and 10.0 for $A = 50$ and 100, respectively; for $B = 20$, $N = 15.2$ and 12.6 for $A = 50$ and 100, respectively. The polynorbornene both solubilizes the aggregated or cross-linked

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Table I
Selected GPC Values for Polynorbornene–Poly[7,8-bis(trifluoromethyl)tricyclo-[4.2.2.0^{2,5}]deca-3,7,9-triene] Block Copolymers (3^{A-B} and 3^{A-B-A})

compd	order[a]	[Cat][b]	cap	$10^{-3}M_w$[c]	$10^{-3}M_n$	M_w/M_n
3^{50-20}	2/1	Mo	PhCHO	13.8	13.1	1.06
3^{50-20}	1/2	Mo	PhCHO	13.2	12.7	1.04
3^{50-20}	2/1	W	PhCHO	13.8	12.8	1.10
3^{50-30}	1/2	Mo	PhCHO	14.2	13.6	1.04
$3^{50-20-50}$		Mo	*t*-BuCHO	28.1	26.8	1.05
$3^{50-20-50}$		W	PhCHO	24.6	23.6	1.06
$3^{50-20-25}$		Mo	*t*-BuCHO	27.4	24.2	1.13
$3^{50-20-10}$		Mo	*t*-BuCHO	21.8	19.9	1.10
$3^{50-20-5}$		Mo	*t*-BuCHO	19.5	17.6	1.11
$3^{25-20-25}$		Mo	PhCHO	14.8	13.6	1.09
$3^{25-20-25}$		Mo	PhCHO	13.8	13.1	1.05
$3^{25-20-25}$		Mo	PhCHO	14.0	13.3	1.06
$3^{25-20-25}$		Mo	PhCHO	15.8	14.6	1.08
$3^{25-10-25}$		Mo	PhCHO	13.6	11.1	1.23
3^{25-10}	2/1	Mo	PhCHO	6.6	5.8	1.14

[a] Order of addition to catalyst, 7,8-bis(trifluoromethyl)tricyclo-[4.2.2.0^{2,5}]deca-3,7,9-triene first (1/2), norbornene first (2/1). [b] Catalyst employed: M(CHCMe$_3$)(NAr)(OCMe$_3$)$_2$, M = Mo or W, Ar = 2,6-C$_6$H$_3$-*i*-Pr$_2$. [c] Versus polystyrene standards.

polyene chains and at the same time regulates how many macromolecules can be assembled in the aggregate.

UV/vis spectra of the diblocks show a broad peak at progressively lower energy as *B* increases, characteristic of a classical form of polyacetylene. However, λ_{max} for 4^{50-20} is ~475 nm, a λ_{max} for a polyene whose conjugation length is ~11 double bonds,[9] not 41. A second peculiarity is that the triblocks (only) show additional peaks characteristic of triene, pentaene, and heptaene conjugation sequences, even in $4^{50-20-50}$ (Figure 1). Additional studies have shown that absorptions for conjugated sequences, containing 3, 5, and 7 double bonds are minimal in $4^{50-20-5}$ and steadily increase in the series $4^{50-20-10}$, $4^{50-20-25}$, and $4^{50-20-50}$. We propose that polyenes that are generated in the large triblocks are restricted in the extent to which their double bonds can be brought into conjugation by twisting of the polyene chain, whereas in the diblocks the polyene chains are relatively mobile and can be brought into conjugation.

Preliminary UV/vis studies using an in-line diode array spectrophotomer have shown that the low and high MW fractions of 4^{50-20} ($4^{50-20-20}$ shows identical behavior) differ only in λ_{max} of the broad absorption; λ_{max} is *blue* shifted by 40 nm in the high molecular weight fraction (Figure 2), consistent with *shorter* conjugated sequences being present in the aggregate than in the macromolecule (on the average).

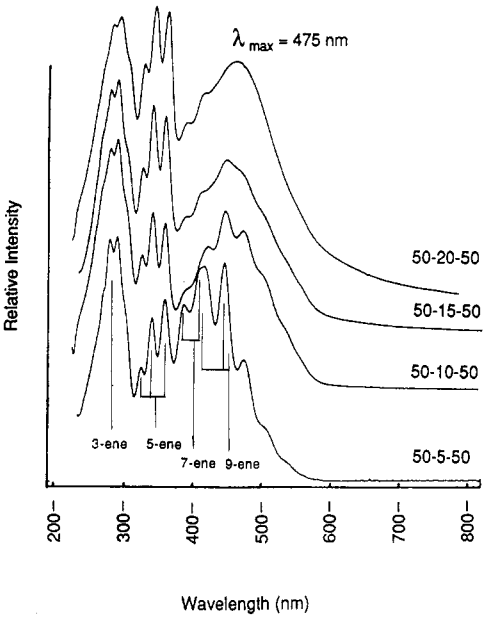

Figure 1. UV/vis spectra of polyNBE–polyene–polyNBE triblock copolymers. (The polyene sequence in the "50–10–50" triblock has an average of approximately 2(10) + 1 double bonds.)

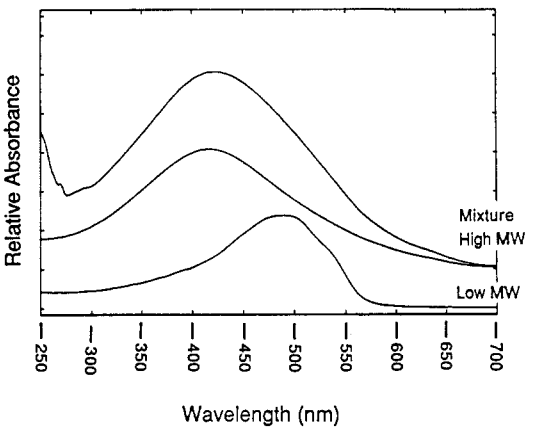

Figure 2. UV/vis spectrum of a 50–20 polyNBE–polyene(41ene) diblock copolymer compared to those of the "high molecular weight" aggregate and "low molecular weight" macromolecule that comprise that copolymer.

In Table III is shown the dependence of the polydispersity of the $4^{25-20-25}$ macromolecules and the aggregates formed from them on concentration of $3^{25-20-25}$ in solution or in the solid state. The polydispersity of the aggregates

Table II
Selected GPC Values for Polynorbornene–Polyene–Polynorbornene Triblocks 4^{A-B-A}, Obtained by Heating Samples of 3^{A-B-A} in Solution at 90 °C for 60 Min

	low MW			high MW				
compd	$10^{-3}M_w$[a]	$10^{-3}M_n$	M_w/M_n	$10^{-3}M_w$	$10^{-3}M_n$	M_w/M_n	% high[c]	N[d]
$4^{100-5-100}$	51.7	46.1	1.12					
$4^{100-10-100}$	50.5	47.7	1.06	433	401	1.08	20	8.4
$4^{100-15-100}$	50.5	47.7	1.06	524	477	1.10	75	10.0
$4^{100-20-100}$	57.4	48.0	1.20	649	605	1.07	90	12.6
$4^{50-5-50}$	19.7	17.8	1.10					
$4^{50-10-50}$	22.8	20.0	1.14				8	
$4^{50-15-50}$	30.5	27.2	1.12	406	366	1.11	67	13.4
$4^{50-20-50}$	29.7	27.8	1.07	473	424	1.11	93	15.2
$4^{25-5-25}$	14.8	12.6	1.18					
$4^{25-10-25}$	15.8	13.0	1.21	185	177	1.04	14	13.6
$4^{25-20-25}$	15.6	14.2	1.10	902	407	2.22	98	28.6
$4^{25-20-25\,b}$	14.7	13.7	1.08	254	199	1.28	50	14.5

[a] Versus polystyrene standards. [b] Heated as a thin film for 60 min at 90 °C. [c] Approximate area of the GPC RI peak for the aggregate relative to the sum of that for the aggregate and that for the macromolecule. [d] High M_n/low M_n.

Scheme I

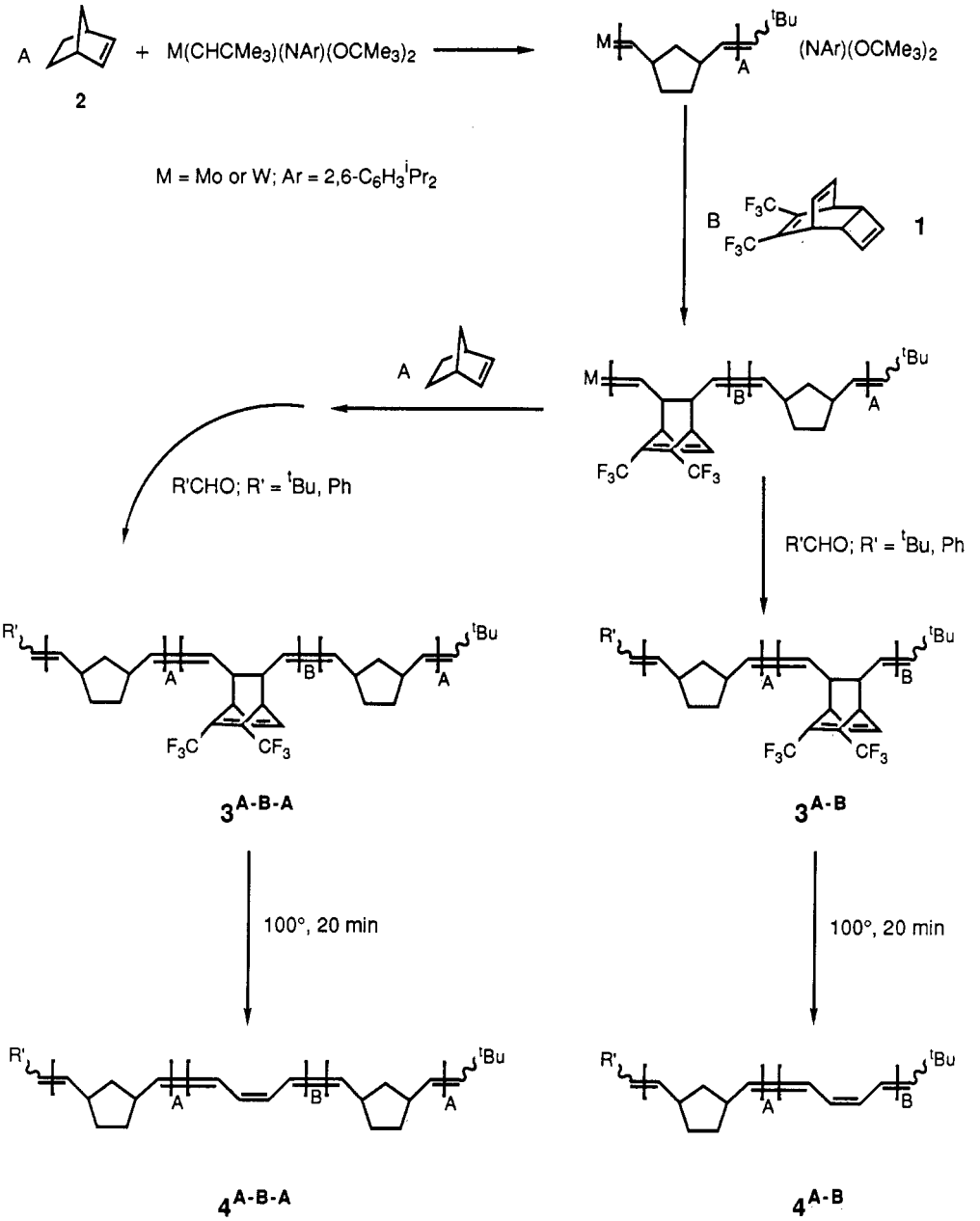

Table III
Results of the Retro-Diels–Alder Reaction at Varying Concentrations of 3^{A-B-A} in Solution and as a Film

		low MW			high MW		
compd	wt %[a]	$10^{-3}M_w$	$10^{-3}M_n$	M_w/M_n	$10^{-3}M_w$	$10^{-3}M_n$	M_w/M_n
$4^{25-20-25}$	0.1	15.2	13.9	1.09	2150	727	2.96
$4^{25-20-25}$	0.5	15.4	14.1	1.09	1750	437	3.33
$4^{25-20-25}$	1.0	15.2	13.9	1.09	207	479	2.66
$4^{25-20-25}$	2.0	15.6	14.2	1.10	902	407	2.22
$4^{25-20-25}$	film	14.7	13.7	1.08	254	199	1.28

[a] wt % = wt(3^{A-B-A})/wt(solvent).

decreases as the concentration of $3^{25-20-25}$ increases, reaching a minimum of 1.28 when the retro-Diels–Alder reaction is performed on a film of $3^{25-20-25}$.

We believe these results are most consistent with the "aggregate" being formed by cross-linking of the polyene portions of the diblocks or triblocks, beginning when the polyene chain length reaches ~15. If this is the case then the implication is that Durham polyacetylene contains a significant amount of cross-linked polyene chains. These results are consistent with other reports that solubilized polyacetylene prepared by classical methods forms "aggregates".[2h,l] The apparent instability of di-*tert*-butyl-capped polyenes having ≥15 double bonds in an unsubstituted backbone[9] provides additional evidence for cross-linking of the polyene chains in these copolymers.

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Registry No. (1)(2) (block copolymer), 114613-37-5; W(CHCMe3)(N(2,6-C6H6-*i*-Pr2))(OCMe3)2, 107440-84-6; Mo-

$(CHCMe_3)(N(2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2):OCMe_3)_2$, 108969-04-6.

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(10) I (4.1 μL, 0.0205 mmol) was added to a solution of $Mo(CHCMe_3)(NAr)(OCMe_3)_2$ (1 mg, 0.00205 mmol) in toluene (1 mL) at −78 °C. After 10 min the solution was warmed and held at −20 °C for 60 min. Pivaldehyde (6 μL, 0.064 mmol) was added and solvents were removed in vacuo while keeping the solution temperature below −20 °C (in order to minimize the retro-Diels–Alder reaction[6]) to give light yellow colored powders quantitatively. Samples were analyzed immediately by GPC in dichloromethane at 25 °C: 5 equiv of 1, M_w = 1370, M_n = 1070, M_w/M_n = 1.28; 10 equiv of 1, M_w = 1700, M_n = 1490, M_w/M_n = 1.15; 20 equiv of 1, M_w = 2600, M_n = 2310, M_w/M_n = 1.13; 20 equiv repeated, M_w = 2400, M_n = 2200, M_w/M_n = 1.10. With time the retro-Diels–Alder reaction yields polyene sequences that alter the hydrodynamic characteristics of poly-1 and lead to higher apparent dispersities.

(11) A solution of norbornene (193 mg, 2.05 mmol) in toluene (10 mL) was added dropwise to a rapidly stirred solution of $Mo(CHCMe_3)(NAr)(OCMe_3)_2$ (20 mg, 0.041 mmol) in toluene (2 mL). After 5 min a solution of 1 (165 μL, 0.82 mmol) in toluene (4 mL) was added dropwise to the rapidly stirred solution. After 5 min another solution of norbornene (193 mg, 2.05 mmol) in toluene (10 mL) was added dropwise to the rapidly stirred solution. After 10 min, 20 μL of benzaldehyde (0.168 mmol) was added. The solvents were removed in vacuo. The residue was dissolved in a minimal amount of methylene chloride and precipitated by addition of excess methanol to obtain light yellow powders essentially quantitatively.

(12) The retro-Diels–Alder reaction was done in solution (methylene chloride or toluene) at 2.0 wt % (polymer weight to solvent weight) or as a thin film. All samples were heated at 90 °C for 60 min. Under these conditions we have shown that the retro-Diels–Alder reaction is complete.[9]

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Electronic Properties of an Electron Donor–Acceptor Polymer Blend

The phase-separation behaviors of organic polymer blends have attracted extensive studies for their effects on mechanical properties,[1] but few studies have been concerned with the relation between the phase-separation structure and the electrical properties. We have been interested in the phase-separation behavior of the photoconductive polymer blends containing electron donor–acceptor (EDA) complexes, because they can have interfaces similar to the p–n junctions of semiconductors and may have unusual electronic properties different from those of doped polymer systems.

Recently, Rodriguez-Parada and Percec reported that polymethacrylates containing a carbazole group as a donor chromophore are miscible with polymethacrylates containing a 3,5-dinitrobenzoyl group as an acceptor.[2] This miscibility was attributed to a relatively weak intermolecular electronic interaction, and the phase separation occurred at 186–230 °C with the concomitant dissociation of the EDA complex.

This finding motivated us to pursue further study on phase-separation behaviors of EDA polymer blends and their effect on photoelectrical properties. We have shown that the phase separation of partly miscible blends of the donor poly[(*N*-ethylcarbazol-3-yl)methyl acrylate] (I) and the acceptor poly[2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate] (II) has a structure similar to the phase structure produced by spinodal decomposition. The effect of this structure on the photocurrent of the polymer blend is also presented.

Polymers I ($\bar{M}_w = 5.0 \times 10^4$) and II ($\bar{M}_w = 3.5 \times 10^4$) were prepared by the radical polymerization of the corresponding monomers[3] by using AIBN as an initiator in benzene. The THF solutions of these polymers were mixed at various ratios, and films were deposited on slide glasses or NESA glasses from the solutions at room temperature. The films are yellow by the EDA complex, which had a UV absorption around 400 nm.

The film of a 1:1 weight ratio of polymers I and II has a phase-separated, matrix–island structure (Figure 1a) in which isolated islands with irregular shapes and sizes (0.5–1 μm) dispersed in the continuous matrix. When this 1:1 film (containing ca. 10 mol % excess of carbazole group) was exposed to iodine vapor for several hours, the islands became green, indicating the formation of an EDA complex between carbazole and iodine. This result suggests that the islands were composed predominantly of the donor polymer and that the matrix was a solid solution of the donor and acceptor polymers with the interchain EDA complex.

When the films were heated, another phase separation started in the matrix, and islands were finally absorbed

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