Macromolecules 1986, *19*, 2108–2114

of star polyimides. IR (KBr) 1780 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{186}H_{90}N_{12}O_{33}$: C, 73.96; H, 3.00; N, 5.56. Found: C, 73.47; H, 3.25; N, 5.86.

Preparation of Biphenylene End-Capped Star Imide Oligomer Having Internal Acetylenes 6b ($\overline{DP}$ = 3). The above procedure was followed, except 0.1731 g (1.040 mmol) of 2-aminobiphenylene was used as an end cap instead of aniline and 0.2 mL × 3 of NMP was used to rinse the end cap. The yield was 0.86 g (88%). IR (KBr) 1775 and 1705 cm^{-1} (C=O, imide). Anal. Calcd for $C_{204}H_{96}N_{12}O_{33}$: C, 75.55; H, 2.98; N, 5.18. Found: C, 74.15; H, 3.20; N, 5.23.

Melt Processing of the Prepolymer (Neat Resin Processing). An appropriate amount of $Ni(CO)_2(PPh_3)_2$ (Aldrich) was added to 200 mg of prepolymer swelled in 50 mL of benzene under Ar. The mixture was stirred for 1 h. The benzene was removed under reduced pressure and the resulting powder was dried at 0.05 mmHg for 18 h.

A modified Wabash hydraulic press (Model 12 10) fitted with Carver heated platens (no. 2102) was used for the neat resin processing. The prepolymer powder (either with or without nickel) was placed in a small pile between 3 in. × 3 in. pieces of copper foil (0.005 in. thick, Baker no. 1-1714) with a 0.005-in. copper foil spacer. The copper foil was washed with 1 N HCl and then with water, prior to use. The assembly was placed in the hydraulic press and melt processed at 325–350 °C under 5000 psi for various times. Plunging the assembly into cold water immediately after processing facilitated removal of the film from the copper foil. Any residual copper that adhered to the surface of the film was removed by placing the film in concentrated ammonium hydroxide for 30 min, followed by a thorough rinsing with water and drying at 110 °C (0.05 mmHg) for 40 h.

Acknowledgment. This research was supported by the Army Research Office, Research Triangle, NC.

Registry No. 1, 102852-93-7; **4b**, 102920-43-4; **4d**, 102940-12-5; $(Ph_3P)_2Ni(CO)_2$, 13007-90-4; 3-$IC_6H_4NH_2$, 626-01-7; $Bu_3SnC{\equiv}CSnBu_3$, 994-71-8.

References and Notes

(1) Hergenrother, P. M. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1984**, *25*(1), 97.

(2) (a) Reppe, W.; Kutepow, N.; Magin, A. *Angew. Chem.* **1969**, *81*, 717; *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 727. (b) Bowden, F. L.; Lever, A. P. B. *Organometal. Chem. Rev.* **1968**, *3*, 227. (c) Hartley, F. R. *Chem. Rev.* **1969**, *69*, 799.

(3) Sefcik, M. D.; Stejskal, E. O.; McKay, R. A.; Schaefer, J. *Macromolecules* **1979**, *12*(3), 423.

(4) Takeichi, T.; Stille, J. K. *Macromolecules*, preceding paper in this issue.

(5) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; p 91.

(6) Sutherlin, D. M.; Stille, J. K.; Alston, W. B. *Macromolecules* **1986**, *19*, 257.

(7) Droske, J. P.; Stille, J. K. *Macromolecules* **1984**, *17*, 1.

(8) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

(9) Droske, J. P.; Gaik, U. M.; Stille, J. K. *Macromolecules* **1984**, *17*, 10.

Readily Processable Imide Oligomers Containing Perfluoroisopropylidene Connecting Units and Reactive Acetylenic and Biphenylene Groups: Synthesis, Curing, and Thermal Properties

Tsutomu Takeichi[†] **and J. K. Stille***

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.
Received January 15, 1986

ABSTRACT: Biphenylene or acetylene end-capped imide oligomers of $\overline{DP}$ = 3, 11 and 22 were prepared by adjusting the stoichiometry of the fluorinated monomers 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane and the end cap. Biphenylene end-capped imide oligomers having internal acetylene in the prepolymer backbone also were prepared similarly with bis(3-aminophenyl)acetylene as an internal acetylene source. Fluorinated star imide oligomers were prepared by utilizing 1,3,5-tris(4-aminophenoxy)benzene as the star point. The prepolymers were soluble in common organic solvents such as benzene, THF, CH_2Cl_2, $CHCl_3$, acetone, and ether and insoluble in hexane and ethanol, although the star prepolymers were less soluble than the linear ones. Melt processing of the prepolymers was carried out with and without the $Ni(PPh_3)_2(CO)_2$ catalyst. Blend melt processing between biphenylene and acetylene end-capped prepolymers also was performed. Prepolymers underwent melt flow to give good films. Films melt processed in the presence of the nickel catalyst were dark brown, while those without the catalyst were light brown and transparent. Melt-processed films showed higher T_g's than the uncured prepolymers and also showed good mechanical properties. Films obtained from prepolymers containing the biphenylene end cap and internal acetylene groups showed excellent thermal properties, considering they have flexible fluorinated groups. The T_g's were above 300 °C and the value for the storage modulus (above T_g) was as high as 2.9 × 10^9 dyn/cm^2 at 411 °C.

Introduction

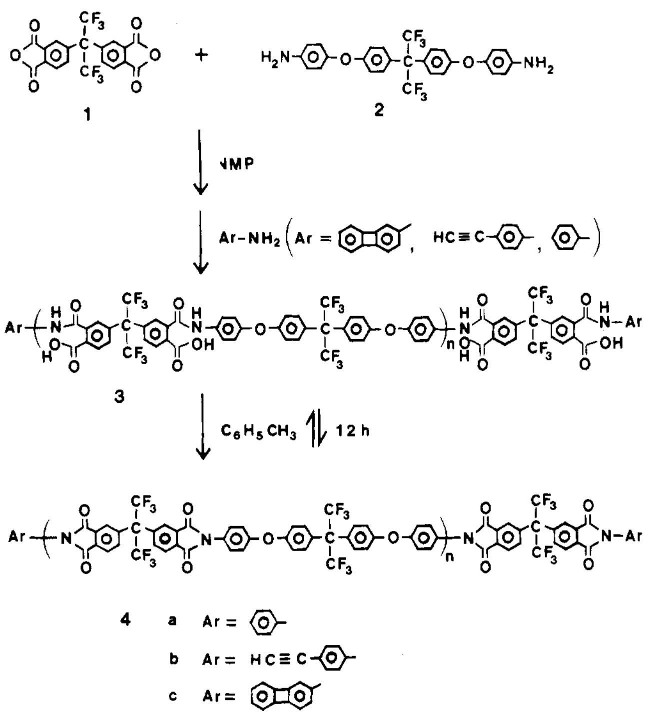
Although polyimides are among the most thermally stable polymers,[1] their insolubility in the common organic solvents results in processing difficulties. One approach to the processable polyimides is the use of reactive groups placed on the ends of soluble oligomers, which could be thermally cured to yield cross-linked polyimides.[2] However, even the low molecular weight oligoimides do not have enough solubility and in most cases precursor amic acid solutions are used for processing. Amic acids are somewhat unstable,[1] especially to water, and the solubility of amic acid requires the use of *N*-methylpyrrolidone or similar high-boiling solvents for solution processing. Isoimide oligomers, which are more soluble than the analogous

---

[†] On leave from School of Materials Science, Toyohashi University of Technology, Toyohashi 440, Japan.

0024-9297/86/2219-2108$01.50/0

Scheme I



imide oligomers, can be converted ultimately to the corresponding imide and thereby provide an alternative to the processing problems.[3] The PMR (polymerization of monomer reactants) approach,[4] which usually utilizes an alcohol solution of monomer reactants, is also widely employed to prepare polyimide composites. Although this approach affords excellent processability, some oligomers may not be properly end-capped, leading to thermal instability. Another approach is the use of flexible monomers, which have soft segments such as methylene, isopropylidene, or hexafluoroisopropylidene groups, thereby providing readily soluble and easily processable polyimides.[5] However, incorporation of the flexible segments lowers the T_g and the mechanical properties above T_g considerably, resulting in a limited use temperature.

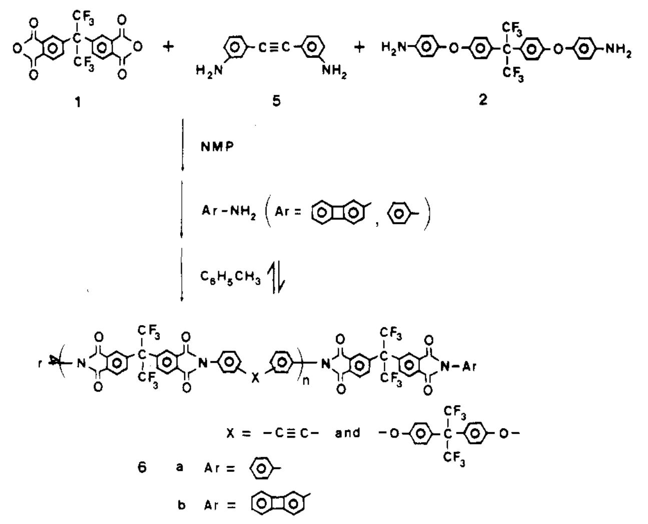
We have shown[6] that by placement of a combination of internal acetylene groups and biphenylene end caps in the imide oligomers, cured polyimide resins with high T_g's and excellent mechanical properties above T_g were achieved. The prepolymers were not soluble, however, once they were cyclodehydrated to oligoimides, even though the precursor amic acids were soluble in some common organic solvents such as THF.

In this paper, we will describe the preparation of easily processable polyimides by the incorporation of flexible perfluorinated groups into the monomers to give processable imide oligomers, which can be cured to highly thermally stable polyimides by applying the combination of internal acetylene and biphenylene end caps.

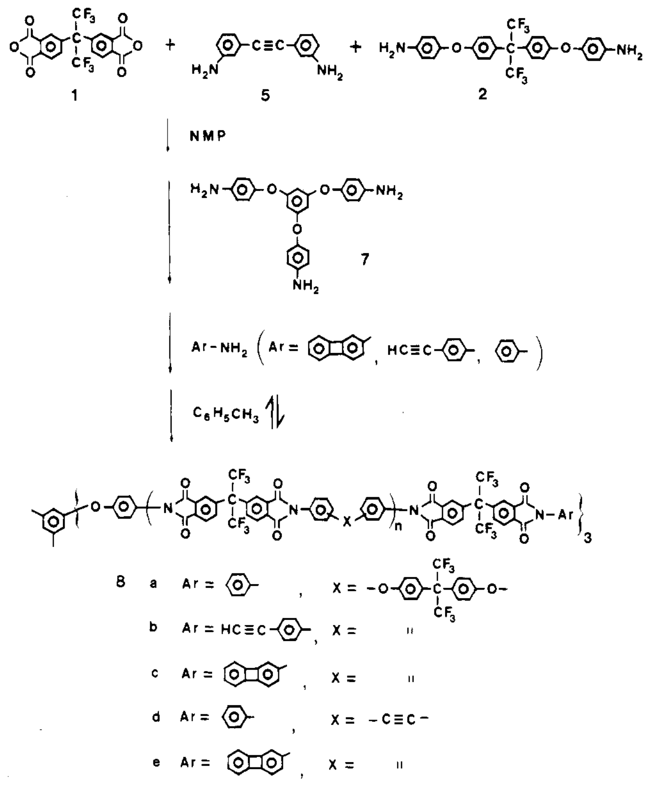
Results and Discussion

Synthesis and Properties of Prepolymers. Biphenylene or acetylene end-capped imide oligomers (**4c** or **4b**), which can be thermally or catalytically cured, were prepared with the fluorinated monomers 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (**1**), and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**2**), according to Scheme I. Phenyl end-capped fluorinated prepolymers (**4a**) were prepared similarly in order to evaluate the effect of the end-capping reagents. The degree of polymerization was controlled by utilizing the appropriate monomer balance according to the equation $\overline{DP} = (1 + r)/(1 + r - 2rp)$.[7] A solution of amic acid **3** was heated in toluene to dehydrocyclize it to imide oligomer **4** which was soluble in toluene and was precipitated into ethanol or aqueous ethanol.

Scheme II



Scheme III



Biphenylene end-capped prepolymers containing internal acetylene units (**6b**), which can produce highly cross-linked polyimides, were prepared by using bis(3-aminophenyl)acetylene (**5**) as an internal acetylene source along with **1** and **2** as comonomers (Scheme II). Phenyl end-capped prepolymers (**6a**) also were prepared to evaluate the role of biphenylene in the curing reaction. Biphenylene, acetylene, and phenyl end-capped star prepolymers (**8**) also were prepared with 1,3,5-tris(4-aminophenoxy)benzene as a star point (Scheme III). When the star amic acid solution in NMP was added to toluene, a small amount of precipitate formed, which, in the case of the prepolymers of low $\overline{DP}$ dissolved by heating to the

Table I
Thermal Transitions of Fluorinated Prepolymers (DSC)

prepolymer	$\overline{DP}$	A/B[a]	T_g, °C	$T_{\text{exo,max}}$ °C
4a	3	0/0	145	
4a	11	0/0	127 (197)[b]	
4a	22	0/0	147 (213)[c]	
4b	3	2/0	150	268
4c	3	0/2	144	362
4c	11	0/2	150 (237)[d]	400
6a	5	2/0	139 (240)[d]	415
6a	11	2/0	137, 231	435
6b	5	2/2	181	353
6b	11	2/2	191 (248)[d]	377
8a	3	0/0	182	
8a	11	0/0	188	
8b	3	3/0	189	305
8b	11	3/0	196	330
8c	3	0/3	192	370
8c	11	0/3	218	370
8d	3	3/0	164	424
8e	3	3/3	164	396

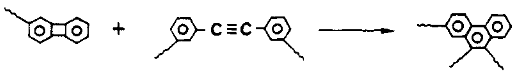
[a] Average number of acetylene groups/biphenylene groups in a molecule. [b] After annealing by heating to 350 °C at the rate of 10 °C/min. [c] After annealing by heating to 400 °C at the rate of 10 °C/min. [d] After annealing by heating at 350 °C for 30 min.

reflux temperature. The higher $\overline{DP}$ prepolymer precipitates did not dissolve in hot toluene. After dehydration in toluene, the imide oligomers were precipitated into ethanol.

The fluorinated imide oligomers are white and soluble in common organic solvents such as ether solvents (THF, dioxane, ether), chlorinated solvents (chloroform, methylene chloride), acetone, DMF, and hydrocarbon solvents (benzene, toluene) and are insoluble in hexane and ethanol, although the star imide oligomers are less soluble than the linear oligomers.

Determination of the thermal transitions of the fluorinated prepolymers (Table I) showed that T_g's of the linear prepolymers **4** were 127–150 °C, while T_g's of the star prepolymer **8** were 164–218 °C. The prepolymers having internal acetylene units (**6b**) had higher T_g's (181–191 °C) as a result of a more rigid main chain. None of the fluorinated prepolymers showed endotherms characteristic of crystalline transitions. Annealing the fluorinated prepolymers at temperatures below the reaction exotherm increased the T_g by 60–100 °C.

Acetylene end-capped prepolymers (**4b** and **8b**) showed exotherms due to the reaction of the end groups at 268–330 °C while the biphenylene end-capped prepolymers (**4c** and **8c**) exhibited exotherms at 362–400 °C. Prepolymers containing the internal acetylenic units and phenyl end caps (**6a** and **8d**) reacted at 415–435 °C, while prepolymers containing internal acetylenic units and biphenylene end caps (**6b** and **8e**) reacted at 353–396 °C, the single exotherm suggesting a selective reaction between internal acetylene units and the biphenyl end cap[8] (eq 1).


(1)

The temperature of the reaction between the internal acetylene and the biphenyl end cap was lower than those reaction temperatures corresponding to the self-reaction of the individual acetylene or biphenylene groups (Figure 1). In the case of linear prepolymers of $\overline{DP}$ = 11, for example, the reaction between the internal acetylene and biphenylene end cap, that for biphenylene alone, and that for internal acetylene units alone were 377, 400, and 435 °C, respectively. The cross-linking reaction of these fluorinated prepolymers occurs at temperatures considerably lower than those of nonfluorinated prepolymers. For example, the temperature of the exothermic maximum for the end-capped biphenylene group on the fluorinated prepolymers is 362–400 °C, while for the nonfluorinated prepolymers it is 420–480 °C.[9] This means that these fluorinated prepolymers are not only soluble in the common organic solvents but can be cured at lower temperatures with or without a catalyst.

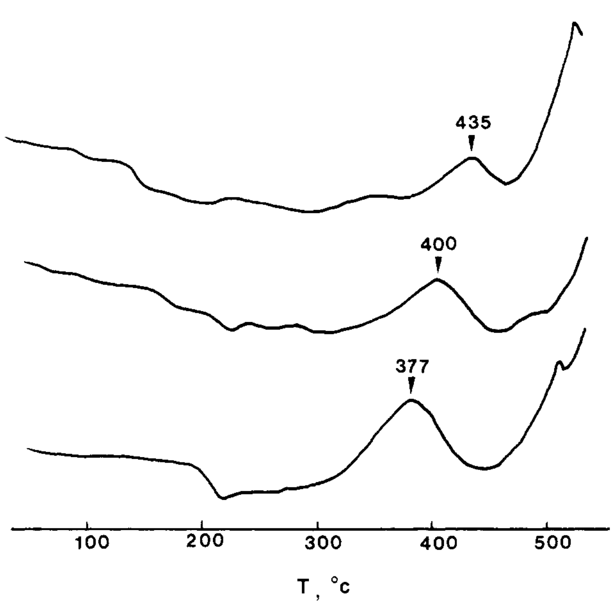


Figure 1. DCS's of prepolymers: top, **6a** (DP = 11); middle, **4c** (DP = 11); bottom, **6b** (DP = 11).

Table II
Thermal Gravimetric Analyses of the Prepolymers

		temp (°C) at % wt loss (air flow)		temp (°C) at % wt loss (N_2 flow)	
prepolymer	$\overline{DP}$	5%	20%	5%	20%
4a	3	385	512	399	527
4a	11	490	521	508	554
4a	22	510	555	510	560
4b	3	498	547	504	560
4c	3	518	554	527	564
4c	11	513	544	510	544
6a	5	480	534	478	544
6a	11	445	528	481	540
6b	5	523	548	525	562
6b	11	503	538	511	546
8a	3	488	531	508	550
8a	11	505	543	510	550
8b	3	488	531	510	551
8b	11	504	540	520	556
8c	3	503	533	520	556
8c	11	497	532	520	558
8e	3	490	519	515	555

The cast films of these fluorinated prepolymers from amic acid (NMP solution) or from imide oligomer (chloroform solution) were too brittle for the determination of modulus vs. temperature (Rheovibron).

TGA analyses of these prepolymers (Table II) show that the fluorinated prepolymers were thermally stable, losing 5% of their weight at 488–523 °C in air and at 504–527 °C under N_2, although the phenyl end-capped prepolymers (**4a**, **6a**, and **8a**) lost 5% of their weight at lower temperatures. Prepolymers of higher $\overline{DP}$ are slightly more thermally stable than those of lower $\overline{DP}$.

Prepolymer Processing and Properties of Cured Films. Neat resin processing of the prepolymers was carried out with and without the catalyst, $Ni(CO)_2(PPh_3)_2$. The prepolymers showed excellent melt flow in most cases,

Table III
Properties of the Melt-Processed Films

prepolymer	$\overline{DP}$	A/B[a]	melt press condn (5000 psi) temp, °C	melt press condn (5000 psi) time, min	cat.	DSC T_g, °C	storage and loss moduli (Rheovibron) E''_{max}, °C	storage and loss moduli (Rheovibron) $10^{-10}E'_{25°C}$, dyn/cm^2	storage and loss moduli (Rheovibron) E'_{lowest},[b] dyn/cm^2
4b	3	2/0	300	20	Ni	208	208	2.9	9.0×10^7 (301 °C)
4b	3	2/0	300	20					
4c	3	0/2	325	20	Ni	222	215	1.5	
4c	11	0/2	350	60	Ni	241	220	2.7	4.4×10^7 (320 °C)
4b/4c	3	2/2	320	20					
6a	5	2/0	350	60	Ni	230			
6a	11	2/0	350	60	Ni				
6b	5	2/2	320	30					
6b	5	2/2	350	10					
6b	5	2/2	350	60	Ni	335	313	1.2	2.9×10^9 (411 °C)
6b	11	2/2	350	60		283	263	2.6	1.5×10^8 (335 °C)
8b	3	3/0	350	90	Ni	244	244	2.2	1.2×10^8 (320 °C)
8b	3	3/0	350	60		250	237	2.6	8.5×10^7 (327 °C)
8b	11	3/0	350	90	Ni	242	225	2.7	6.6×10^7 (345 °C)
8b	11	3/0	350	60		251	231	2.6	5.7×10^7 (321 °C)
8c	3	0/3	350	90	Ni	248	243	2.7	9.4×10^7 (320 °C)
8c	3	0/3	350	60		235,275	254	1.9	7.6×10^7 (311 °C)
8c	11	0/3	350	90	Ni	238	231	2.7	7.1×10^7 (330 °C)
8c	11	0/3	350	60		251	233	2.4	6.9×10^7 (330 °C)
8b/8c	3	3/3	350	60		247	234	2.7	9.7×10^7 (335 °C)
8b/8c	11	3/3	350	60		246	225	2.7	6.2×10^7 (313 °C)
8d	3	3/0	350	60	Ni	233	258	2.3	2.8×10^8 (338 °C)
8e	3	3/3	350	20		283,314	308	3.0	2.5×10^9 (351 °C)
8e	3	3/3	350	60	Ni	270	304	1.6	4.9×10^8 (426 °C)

[a] Average number of acetylene groups/biphenylene groups in a molecule. [b] Lowest value of the storage modulus at the temperature indicated.

but in some melt flow was excessive at the cure temperature. Curing with the nickel catalyst restricted the melt flow to some extent because of the faster curing rate. In this way, films could be made in the presence of the nickel catalyst for the prepolymers that could not be melt processed into films without the nickel catalyst. Films cured with a nickel catalyst were dark brown and somewhat transparent, and those cured without the catalyst were light brown and transparent.

When the acetylene end-capped prepolymer **4b** ($\overline{DP}$ = 3), whose exothermic maximum appeared at 268 °C, was cured in a DSC cap by heating to 300 °C (10 °C/min) and then quenched, the cured prepolymer had a T_g at 217 °C and the exotherm disappeared. Melting processing **4b** ($\overline{DP}$ = 3) without the nickel catalyst did not yield a film as a result of excessive melt flow. Therefore, melt processing was effected in the presence of 10 wt % $Ni(CO)_2(PPh_3)_2$ (12.2 mol % based on acetylene) at 300 °C for 20 min under 5000 psi to give a film with a T_g of 208 °C, which is 58 °C higher than that of the prepolymer. The mechanical strength of this film dropped remarkably above T_g (Table III and Figure 2).

Biphenylene end-capped prepolymer **4c** ($\overline{DP}$ = 3), whose exotherm did not disappear at all by heating to 330 °C (10 °C/min) in a DSC cap, was melt processed with 10 wt % $Ni(CO)_2(PPh_3)_2$ (12 mol % based on biphenylene), which dropped the exothermic maximum to 286 °C. A poor-quality film was obtained that had T_g = 215 °C. The melt processing of a biphenylene end-capped prepolymer of higher $\overline{DP}$, **4c** ($\overline{DP}$ = 11), gave a good film whose T_g was 220 °C (70 °C above the T_g of the prepolymer). The mechanical strength of this cured film dropped above T_g, reaching a lowest value, 4.4×10^7 dyn/cm^2, at 320 °C.

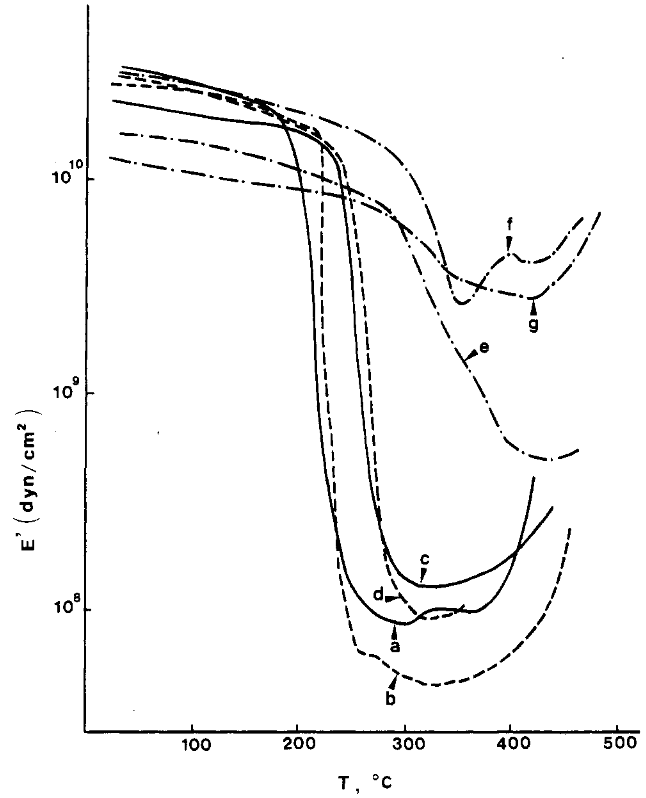


Figure 2. Thermomechanical properties of melt-processed films: (a) **4b** (DP = 3) (Ni catalyst); (b) **4c** (DP = 11) (Ni catalyst); (c) **8b** (DP = 3) (Ni catalyst); (d) **8c** (DP = 3) (Ni catalyst); (e) **8e** (DP = 3) (Ni catalyst); (f) **8e** (DP = 3); (g) **6b** (DP = 5) (Ni catalyst).

The star prepolymers having acetylene or biphenylene end groups (**8b** and **8c**) also were melt processed to form films of high quality either in the presence or the absence of a nickel catalyst (20 mol % nickel catalyst based on the end groups, 2.6 wt % for $\overline{DP}$ = 3 and 0.8 wt % for $\overline{DP}$ = 11). The prepolymers of lower $\overline{DP}$ formed films having better thermomechanical properties based on the values of storage moduli above T_g (Table III). Curing in the presence of the nickel catalyst had little effect on the T_g of the cured films, all the films of **8b** and **8c** having T_g's between 225–254 °C. Films obtained with the nickel catalyst showed slightly better thermomechanical properties than those without the catalyst, however. The star prepolymers gave cured films of slightly higher T_g than those of linear prepolymers, but the thermomechanical properties were not much improved by the introduction of a star point. In fact, a dramatic drop in modulus above T_g was observed for the cured star prepolymers. [Figure 2, compare c, d (star) and a,b (linear)].

The attempt was made to cure a blend of acetylene and biphenylene end-capped prepolymers by melt pressing a mixture and generating a phenanthrene cross-link site. The melt processing of a linear combination (**4b**/**4c**) without the nickel catalyst failed to make a film because of excessive melt flow, but melt processing of star combinations (**8b**/**8c**) formed films of good quality without the catalyst. The thermal properties of the blend melt-processed films, however, were almost the same as the individually melt-processed films.

Prepolymers having acetylene groups in the backbone of the main chain were melt processed with and without the nickel catalyst. For the linear prepolymer end capped with phenyl groups (**6a**), excessive melt flow prevented the formation of films of good quality, even in the presence of the nickel catalyst. A star prepolymer containing phenyl end groups (**8d**) was melt processed with the catalyst, giving films having good thermal properties; T_g = 258 °C and the value for the storage modulus at 338 °C was 2.8×10^8 dyn/cm^2. The thermal properties of melt-processed films of **8d** were almost the same as for the films from the acetylene end-capped star prepolymer **8b** ($\overline{\mathrm{DP}} = 3$).

The star prepolymer with biphenylene end groups (**8e**) was melt processed with and without the catalyst. By the appropriate combination of biphenylene end groups and internal acetylene units, both films displayed remarkably improved thermal properties, showing T_g's above 300 °C and maintaining their mechanical properties above T_g (Figure 2, e and f). Especially interesting is the melt-processed film formed from **8e** without the catalyst, since it maintained a relatively high storage modulus, 2.5×10^9, at 351 °C.

In the presence of a nickel catalyst, biphenylene end-capped linear prepolymer **6b** formed a brittle film with a T_g at 313 °C, the highest obtained for this fluorinated polyimide series. The thermomechanical properties also were impressive, as this polymer maintained a relatively high storage modulus, 2.9×10^9 dyn/cm^2 at 411 °C. The film obtained from **8e** in the absence of a nickel catalyst showed better thermomechanical properties than that with the catalyst (E'_{lowest} was 2.5×10^9 dyn/cm^2 for the film without the catalyst and 4.9×10^8 with the catalyst). The same was true for the films obtained from nonfluorinated biphenylene end-capped polyimides having internal acetylenic groups.[6]

The excellent thermal properties of **6b** ($\overline{\mathrm{DP}} = 5$) and **8e** ($\overline{\mathrm{DP}} = 3$) evidently are a result of the selective reaction between the biphenylene end groups and the internal acetylene groups to form the phenanthrene structure. The fact that the film of **6b** ($\overline{\mathrm{DP}} = 5$) was much superior to **6b** ($\overline{\mathrm{DP}} = 11$) illustrates the importance of cross-link density. Since **6b** ($\overline{\mathrm{DP}} = 5$) and **6b** ($\overline{\mathrm{DP}} = 11$) have the same number of cross-linking sites in the average oligomer (two internal acetylenes and two biphenylene end caps), it is apparent that cross-link density of **6b** ($\overline{\mathrm{DP}} = 5$) is considerably higher than that of **6b** ($\overline{\mathrm{DP}} = 11$).

Table IV
TGA of the Melt-Processed Films

prepolymer	$\overline{\mathrm{DP}}$	cat.	temp (°C) at % wt loss (air flow) 5%	temp (°C) at % wt loss (air flow) 20%	temp (°C) at % wt loss (N_2 loss) 5%	temp (°C) at % wt loss (N_2 loss) 20%
4b	3	Ni	355	483	364	472
4c	3	Ni	440	530	455	550
6b	11		477	513	510	548
8b	3	Ni	488	538	508	553
8b	3		478	524	510	545
8b	11	Ni	479	528	511	554
8b	11		488	526	506	541
8c	3	Ni	480	531	509	554
8c	11	Ni	484	533	509	552
8b/8c	3		488	533	512	547
8b/8c	11		484	527	508	543
8e	3		496	524	513	555

TGA analyses of the melt-processed films (Table IV) show that all the films, except the linear end-capped prepolymers (**4b** and **4c**), lost 5% of their weight at 477–496 °C under air and at 506–513 °C under nitrogen.

Conclusions

Fluorinated imide oligomers having biphenylene or acetylene end caps, along with those having internal acetylene and biphenylene end caps, were prepared in order to obtain soluble and easily processable materials. The fluorinated prepolymers had good solubility in the common organic solvents such as ether solvents (THF), chlorinated solvents (chloroform), ketone solvents (acetone), and amide solvents (DMF). Melt processing biphenylene end-capped prepolymers having internal acetylenic units gave films having excellent thermal properties, as a result of the efficient cross-linking reaction between the internal acetylenes and the biphenylene end caps to generate phenanthrene cross-links. The T_g's were above 300 °C and the mechanical properties were maintained above T_g.

Experimental Section

All melting points are uncorrected. Infrared spectra were measured with a Beckman 4240 spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc. ^1H and ^{13}C NMR spectra were measured with a Varian EM-360 spectrometer or an IBM WP-270 spectrometer. All chemical shifts are expressed in ppm downfield from internal tetramethylsilane.

Thermal analyses were performed with a Du Pont 990 thermal analyzer equipped with a differential scanning calorimeter (DSC) cell base (heating rate, 10 °C/min). A Du Pont 951 thermogravimetric analyzer (TGA) was used for thermal stability tests (heating rate, 5 °C/min). Dynamic thermomechanical analyses were obtained on a Rheovibron DDV-II-C dynamic viscoelastometer (frequency, 35 Hz).

2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (**1**) (American Hoechst) and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**2**) (Alfa) were obtained commercially and purified by recrystallization[5b] or sublimation. Bis(3-aminophenyl)acetylene[6] (**5**) and 1,3,5-tris(4-aminophenoxy)benzene[9] (**7**) were prepared according to the procedures described previously.

Neat resin processing of the imide oligomers were carried out according to the procedure reported previously.[6]

Phenyl End-Capped Imide Oligomer 4a ($\overline{\mathrm{DP}} = 1$). To 2 mL of distilled NMP was added 0.7996 g (1.800 mmol) of **1** under Ar. Solution of the dianhydride was effected by heating the mixture to 90 °C with mechanical stirring. The solution was kept at 50 °C, and 0.4023 g (4.320 mmol) of aniline was added. Heating was continued for 1 h, at which time the solution was added dropwise to 30 mL of toluene and heated to the reflux temperature with a Dean–Stark apparatus for 10 h. The toluene was removed at reduced pressure and the polyimide in NMP was added dropwise into 100 mL of ethanol (a precipitate did not form). To the NMP–ethanol solution was added 100 mL of water to precipitate a white powder, which turned oily by continued stirring. The mixture was left overnight to solidify the precipitate. The white solid was filtered and dried at 110 °C (0.05 mmHg) for 40 h to yield 0.84 g (78%) of **4a** ($\overline{DP}$ = 1). IR (KBr) 1785 and 1720 cm^{-1} (C=O, imide). Anal. Calcd for $C_{31}H_{16}N_2F_6O_4$: C, 62.63; H, 2.71; N, 4.71. Found: C, 62.77; H, 2.76; N, 4.70.

Phenyl End-Capped Imide Oligomer 4a ($\overline{DP}$ = 3). To 0.6219 g (1.400 mmol) of **1** dissolved in 2 mL of NMP was added 0.3629 g (0.700 mmol) of **2** in 0.6 mL of NMP dropwise under Ar. An additional 0.2 mL × 2 of NMP was used to ensure complete transfer of the monomer. The solution was heated at 50 °C for 30 min, at which time 0.156 g (1.68 mmol, 20% excess) of aniline was added and the mixture was heated for 1 h. The solution was added into 30 mL of toluene and heated to reflux in a Dean–Stark apparatus for 10 h. The toluene solution was added to 150 mL of ethanol, and 50 mL of water was added to precipitate a white powder. The fine powder was filtered and dried at 110 °C (0.05 mmHg) for 40 h to yield 0.71 g (67%) of **4a** ($\overline{DP}$ = 3). IR (KBr) 1785 and 1730 cm^{-1} (C=O, imide). Anal. Calcd for $C_{77}H_{38}N_4F_{18}O_{10}$: C, 60.80; H, 2.52. Found: C, 59.67; H, 2.93.

Phenyl End-Capped Imide Oligomer 4a ($\overline{DP}$ = 11). The above procedure was followed, except 0.4442 g (1.000 mmol) of **1**, 0.4401 g (0.8489 mmol) of **2**, and 0.048 g (0.51 mmol) of aniline were used to yield 0.75 g (85%) of **4a** ($\overline{DP}$ = 11). IR (KBr) 1785 and 1730 cm^{-1} (C=O, imide). Anal. Calcd for $C_{261}H_{126}N_{12}F_{66}O_{34}$: C, 59.97; H, 2.43. Found: C, 59.26; H, 2.98.

Phenyl End-Capped Imide Oligomer 4a ($\overline{DP}$ = 22). The above procedure was followed, except 0.4442 g (1.000 mmol) of **1**, 0.4827 g (0.931 mmol) of **2**, and 0.025 g (0.27 mmol) of aniline were used to yield 0.67 g (74%) of **4a** ($\overline{DP}$ = 22). IR (KBr) 1790 and 1735 cm^{-1} (C=O, imide). Anal. Calcd for $C_{514}H_{247}N_{23}F_{132}O_{67}$: C, 59.80; H, 2.41. Found: C, 59.52; H, 2.66.

Acetylene End-Capped Imide Oligomer 4b ($\overline{DP}$ = 3). The above procedure was followed, except 0.6219 g (1.400 mmol) of **1**, 0.3629 g (0.700 mmol) of **2**, and 0.180 g (1.54 mmol) of 4-ethynylaniline[9] were used to yield 0.62 g (57%) of **4b** ($\overline{DP}$ = 3). IR (KBr) 1785 and 1725 cm^{-1} (C=O, imide). Anal. Calcd for $C_{81}H_{38}N_4F_{18}O_{10}$: C, 62.00; H, 2.44. Found: C, 59.51; H, 2.68.

Biphenylene End-Capped Imide Oligomer 4c ($\overline{DP}$ = 3). The above procedure was followed, except 0.6219 g (1.400 mmol) of **1**, 0.3629 g (0.700 mmol) of **2**, and 0.258 g (1.54 mmol) of 2-aminobiphenylene[10] were used to yield 0.82 g (70%) of **4c** ($\overline{DP}$ = 3). IR (KBr) 1785 and 1730 cm^{-1} (C=O, imide). Anal. Calcd for $C_{89}H_{42}N_4F_{18}O_{10}$: C, 64.04; H, 2.54. Found: C, 62.31; H, 2.72.

Biphenylene End-Capped Imide Oligomer 4c ($\overline{DP}$ = 11). The above procedure was followed, except 0.4442 g (1.000 mmol) of **1**, 0.4401 g (0.8489 mmol) of **2**, and 0.0669 g (0.400 mmol) of 2-aminobiphenylene[10] were used to yield 0.77 g (85%) of **4c** ($\overline{DP}$ = 11). IR (KBr) 1780 and 1720 cm^{-1} (C=O, imide). Anal. Calcd for $C_{273}H_{130}N_{12}F_{66}O_{34}$: C, 60.99; H, 2.44; N, 3.13. Found: C, 60.73; H, 2.49; N, 3.28.

Phenyl End-Capped Imide Oligomer Having Internal Acetylenes 6a ($\overline{DP}$ = 5). The above procedure was followed, except 0.6664 g (1.500 mmol) of **1**, 0.2083 g (1.000 mmol) of **5**, and 0.140 g (1.50 mmol) of aniline were used to yield 0.31 g (34%) of **6a** ($\overline{DP}$ = 5). IR (KBr) 1780 and 1720 cm^{-1} (C=O, imide). Anal. Calcd for $C_{97}H_{44}N_6F_{18}O_{12}$: C, 63.75; H, 2.43; N, 4.60. Found: C, 64.33; H, 2.68; N, 5.18.

Phenyl End-Capped Imide Oligomer Having Internal Acetylenes 6a ($\overline{DP}$ = 11). The above procedure was followed, except 0.5233 g (1.178 mmol) of 1, 0.3111 g (0.600 mmol) of **2**, 0.0833 g (0.400 mmol) of **5**, and 0.056 g (0.60 mmol) of aniline were used to yield 0.56 g (62%) of **6a** ($\overline{DP}$ = 11). IR (KBr) 1780 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{235}H_{110}N_{12}F_{54}O_{30}$: C, 61.26; H, 2.41; N, 3.65. Found: C, 61.63; H, 2.69; N, 4.25.

Biphenylene End-Capped Imide Oligomer Having Internal Acetylenes 6b ($\overline{DP}$ = 5). The above procedure was followed, except 0.6664 g (1.500 mmol) of **1**, 0.2083 g (1.000 mmol) of **5**, and 0.1839 g (1.100 mmol, 10% excess) of 2-aminobiphenylene[10] were used to yield 0.71 g (72%) of **6b** ($\overline{DP}$ = 5). IR (KBr) 1775 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{109}H_{48}N_6F_{18}O_{12}$: C, 66.27; H, 2.45; N, 4.25. Found: C, 66.00; H, 2.49; N, 4.26.

Biphenylene End-Capped Imide Oligomer Having Internal Acetylenes 6b ($\overline{DP}$ = 11). The above procedure was followed, except 0.5233 g (1.178 mmol) of **1**, 0.3111 g (0.600 mmol) of **2**, 0.0833 g (0.400 mmol) of **5**, and 0.0803 g (0.480 mmol) of 2-aminobiphenylene[10] were used to yield 0.63 g (66%) of **6b** ($\overline{DP}$ = 11). IR (KBr) 1775 and 1720 cm^{-1} (C=O, imide). Anal. Calcd for $C_{247}H_{114}N_{12}F_{54}O_{30}$: C, 62.38; H, 2.42; N, 3.53. Found: C, 62.09; H, 2.47; N, 3.49.

Phenyl End-Capped Star Imide Oligomer 8a ($\overline{DP}$ = 3). The above procedure was followed, using 0.5331 g (1.200 mmol) of 1, 0.3111 g (0.600 mmol) of **2**, 0.0799 g (0.200 mmol) of **7**, and 0.084 g (0.90 mmol) of aniline. After the cyclodehydration in toluene, the solution was precipitated in ethanol to yield 0.68 g (72%) of **8a** ($\overline{DP}$ = 3). IR (KBr) 1780 and 1720 cm^{-1} (C=O, imide). Anal. Calcd for $C_{237}H_{114}H_{12}F_{54}O_{33}$: C, 60.78; H, 2.45; N, 3.59. Found: C, 60.51; H, 2.48; N, 3.57.

Phenyl End-Capped Star Imide Oligomer 8a ($\overline{DP}$ = 11). The above procedure was followed, using 0.4710 g (1.060 mmol) of **1**, 0.4666 g (0.900 mmol) of **2**, 0.024 g (0.060 mmol) of **7**, and 0.25 g (0.30 mmol) of aniline to yield 0.74 g (78%) of **8a** ($\overline{DP}$ = 11). IR (KBr) 1780 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{789}H_{378}N_{36}F_{198}O_{105}$: C, 59.97; H, 2.41; N, 3.19. Found: C, 60.24; H, 2.49; N, 3.22.

Acetylene End-Capped Star Imide Oligomer 8b ($\overline{DP}$ = 3). The above procedure was followed, except 0.5331 g (1.200 mmol) of 1, 0.3111 g (0.600 mmol) of **2**, 0.0799 g (0.200 mmol) of **7**, and 0.0843 g (0.720 mmol) of 4-ethynylaniline were used to yield 0.82 g (86%) of **8b** ($\overline{DP}$ = 3). IR (KBr) 1780 and 1720 cm^{-1} (C=O, imide). Anal. Calcd for $C_{243}H_{114}N_{12}F_{54}O_{33}$: C, 61.37; H, 2.42; N, 3.53. Found: C, 60.43; H, 2.49; N, 3.43.

Acetylene End-Capped Star Imide Oligomer 8b ($\overline{DP}$ = 11). The above procedure was followed, except 0.4710 g (1.060 mmol) of 1, 0.4666 g (0.900 mmol) of **2**, 0.0240 g (0.0600 mmol) of **7**, and 0.0253 g (0.216 mmol) of 4-ethynylaniline were used to yield 0.83 g (87%) of **8b** ($\overline{DP}$ = 11). IR (KBr) 1780 and 1720 cm^{-1} (C=O, imide). Anal. Calcd for $C_{795}H_{378}N_{36}F_{198}O_{105}$: C, 60.15; H, 2.40; N, 3.18. Found: C, 59.51; H, 2.42; N, 3.08.

Biphenylene End-Capped Star Imide Oligomer 8c ($\overline{DP}$ = 3). The above procedure was followed, except 0.5331 g (1.200 mmol) of **1**, 0.3111 g (0.600 mmol) of **2**, 0.0799 g (0.200 mmol) of **7**, and 0.1204 g (0.720 mmol) of 2-aminobiphenylene[10] were used to yield 0.78 g (79%) of **8c** ($\overline{DP}$ = 3). IR (KBr) 1775 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{255}H_{120}N_{12}F_{54}O_{33}$: C, 62.43; H, 2.47; N, 3.43. Found: C, 61.26; H, 2.44; N, 3.40.

Biphenylene End-Capped Star Imide Oligomer 8c ($\overline{DP}$ = 11). The above procedure was followed, except 0.4710 g (1.060 mmol) of **1**, 0.4666 g (0.900 mmol) of **2**, 0.0240 g (0.0600 mmol) of 7, and 0.0361 g (0.216 mmol) of 2-aminobiphenylene[10] were used to yield 0.82 g (85%) of **8c** ($\overline{DP}$ = 11). IR (KBr) 1775 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{807}H_{384}N_{36}F_{198}O_{105}$: C, 60.48; H, 2.42; N, 3.15. Found: C, 60.57; H, 2.47; N, 3.15.

Phenyl End-Capped Star Imide Oligomer Having Internal Acetylenes 8d ($\overline{DP}$ = 3). The above procedure was followed, except 0.6664 g (1.500 mmol) of 1, 0.1562 g (0.7500 mmol) of **5**, 0.0999 g (0.250 mmoll) in **7**, and 0.0768 g (0.825 mmol) of aniline were used to yield 0.41 g (44%) of **8d** ($\overline{DP}$ = 3). IR (KBr) 1780 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{198}H_{90}N_{12}O_{27}F_{56}$: C, 63.37; H, 2.42; N, 4.48. Found: C, 62.91; H, 2.55; N, 4.77.

Biphenylene End-Capped Star Imide Oligomer Having Internal Acetylenes 8e ($\overline{DP}$ = 3). The above procedure was followed, except 0.138 g (0.825 mmol) of 2-aminobiphenylene[10] was used instead of aniline to yield 0.76 g (76%) of **8e** ($\overline{DP}$ = 3). IR (KBr) 1780 and 1715 cm^{-1} (C=O, imide). Anal. Calcd for $C_{216}H_{96}N_{12}F_{36}O_{27}$: C, 65.27; H, 2.43; N, 4.23. Found: C, 64.17; H, 2.48; N, 4.26.

Acknowledgment. This research was supported by the Army Research Office, Research Triangle, NC.

Registry No. 1, 1107-00-2; **4a** ($n = 1$), 102852-94-8; **4a**, 102920-40-1; **4b**, 102920-41-2; **4c**, 102920-42-3; **6a**, 102920-39-8; **6b**, 102920-38-7; $(Ph_3P)_2Ni(CO)_2$, 13007-90-4; $C_6H_5NH_2$, 62-53-3.

References and Notes

(1) Hergenrother, P. M.; Johnston, N. J. *Resins for Aerospace*; American Chemical Society: Washington, DC, 1980; *ACS Symp. Ser. No. 132*.

(2) Hergenrother, P. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1984**, *25*(1), 97.

(3) Landis, A. L.; Naselow, A. B. *High Temperature Polymer Matrix Comosites*, NASA Conference Publication 2385, 1983; p 11.

(4) (a) Serafini, T. T.; Delvigs, P.; Lightsey, G. R. *J. Appl. Polym. Sci.* **1972**, *16*, 905. (b) Serafini, T. T.; Delvigs, P.; Lightsey, G. R. U.S. Patent 3 745 149, July, 1973. (c) Serafini, T. T.; Delvigs, P.; Alston, W. B. "PMR Polyimides-Review and Update"; NASA TM-82821, 1982, and Proceedings of the 27th National SAMPE Symposium and Exhibition, May, 1982.

(5) (a) Jones, R. J.; Chang, G. E.; Powell, S. H.; Green, H. E. *High Temperature Polymer Matrix Composites*; NASA Conference Publication 2385, 1983; p 271. (b) Rogers, F. E. U. S. Patent 3 356 648, Dec, 1967. (c) Harris, F. W.; Sridhar, K.; Das, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1984**, *25*(1), 110.

(6) Takeichi, T.; Stille, J. K. *Macromolecules* **1986**, *19*, 2103.

(7) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; p 91.

(8) Friedman, L.; Rabideau, P. W. *J. Org. Chem.* **1968**, *33*, 451.

(9) Takeichi, T.; Stille, J. K. *Macromolecules* **1986**, *19*, 2093.

(10) Droske, J. P.; Gaik, U. M.; Stille, J. K. *Macromolecules* **1984**, *17*, 10.

(11) Coe, D. G. U.S. Patent 3 310 573, Mar 1967.

Synthesis and Characterization of Polyurethane–Diacetylene Segmented Copolymers

M. F. Rubner*

GTE Laboratories Incorporated, Waltham, Massachusetts 02254.

Received December 12, 1985

ABSTRACT: Polyurethane segmented copolymers containing the reactive diacetylene group within the hard segments were synthesized from three basic monomers: a low molecular weight hydroxyl-terminated polyether, a diacetylenediol, and a diisocyanate. Thermal and spectroscopic analysis revealed a two-phase domain structure in which the diacetylene groups reside in hard-segment domains dispersed throughout a continuous matrix of the flexible soft-segment material. In such an arrangement, the diacetylene units can be cross-polymerized to the poly(diacetylene) form within these domains (via heat or radiation) without disruption of the flexible nature of the elastomeric phase. The result is a material that exhibits the optical properties of a poly(diacetylene) and the mechanical properties of a tough highly extensible elastomer. The thermal–mechanical properties of the elastomers could be dramatically modified by cross-polymerization of the diacetylene groups. The polyurethane–diacetylene elastomers represent a new class of materials with a unique combination of mechanical and optical properties.

I. Introduction

The topochemical solid-state polymerization of diacetylene monomers to fully conjugated polymers with extended chain geometries has been exploited with increasing zeal over the past 10 years in an effort to prepare polymeric systems with novel electrical, optical, and mechanical properties.[1] The fully extended unsaturated backbone of the poly(diacetylenes) gives rise to many of the novel properties of these materials such as their nonlinear optical properties,[2] thermochromic properties,[3] and highly anisotropic mechanical properties.[4] Although the backbone structure is primarily responsible for the optical and electrical properties of these unique materials, it is becoming increasingly more evident that dramatic changes in the behavior of these polymers can be introduced by the manipulation of the structure of their side groups. Thus, by varying the composition and organization of the side groups, it is possible to obtain a wide variety of diacetylene polymers with a broad range of physical properties. However, even with this tremendous capability to molecularly engineer the properties of the poly(diacetylenes) via manipulation of their side groups, the construction of a poly(diacetylene) with the optimum combination of optical, mechanical, and processing behaviors has not been realized. Indeed, a highly desirable material would be a polymer exhibiting the novel optical properties of a poly(diacetylene) and the mechanical behavior of a tough, highly extensible elastomer or fiber.

In addition to the polymerization of the monomeric diacetylenes, it has been demonstrated that the diacetylene functionality can be incorporated in the repeat structure of a polymer backbone and will undergo solid-state cross-polymerization on exposure to suitable radiation or by annealing at elevated temperatures.[5-8] In this case, the resultant side groups are actually polymer chains connecting the poly(diacetylene)-conjugated backbones in a networklike structure. These materials have recently been referred to as macromonomers[7] due to the systematic polymerization of the diacetylene units within the backbone of the host polymer, giving rise to this final networklike structure. The term cross-polymerized[7] is used to indicate that polymer chains are formed at regular intervals along the original polymer backbone as opposed to the typical random cross-linking that many polymers undergo when exposed to radiation. Recently, this approach has been extended to segmented copolymers[9,10] in which the cross-polymerization reaction can be restricted to phase-separated domains containing the diacetylene groups. While a number of different macromonomers have been synthesized and subsequently cross-polymerized, a detailed investigation of the structure–property relationships in these novel materials has not emerged. This is unfortunate since it is expected that with the right combination of structure and molecular organization, these materials would exhibit extremely interesting optical properties and novel mechanical behavior. The properties

---

* Current address: Department of Materials Science and Engineering, MIT, Cambridge, MA 02139.