species and hence its propagation rate constant (k_p) in cationic polymerization. Stopped-flow spectroscopy has successfully been applied to the determination.

Acknowledgment. Financial support from the Ministry of Education, Japanese Government is gratefully acknowledged.

References and Notes

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Acetylene Terminated Phenyl-*as*-triazine Oligomers and Polymers Therefrom[1a]

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ABSTRACT: Acetylene-terminated phenyl-*as*-triazine oligomers (ATPT) were prepared by two methods. Method 1 involved the preparation of amidrazone-terminated phenyl-*as*-triazine oligomers which were subsequently end capped with 4-(4-ethynylphenoxy)benzil to yield ATPT. Method 2 involved the direct preparation of ATPT from the reaction of the diamidrazone, the bisbenzil, and 4-(4-ethynylphenoxy)benzil. The ATPT prepared by method 2 exhibited better solubility, higher heats of reaction, lower polymer melt temperatures, and after thermal cure higher glass transition temperatures than those prepared by method 1. Preliminary adhesive and composite work was performed with one ATPT. Two acetylene-containing phenyl-*as*-triazine model compounds were prepared and characterized by high-pressure liquid chromatography and mass spectroscopy. The thermal reactions of the two model compounds were studied.

Linear polyphenyl-*as*-triazines are high-temperature thermoplastics with good long-term thermooxidative stability at 533 K (260 °C).[2a] However, at 533 K under load, these polymers undergo thermoplastic deformation. Previous attempts to thermally cross-link these polymers through nitrile and cyanato groups located on the pendant phenyl group attached to the *as*-triazine ring were only moderately successful.[2b] The polymers containing the cyanato groups were not processable due to the fast reaction of the cyanato groups. Whereas high temperatures were required to induce reaction of the nitrile groups which resulted in thermal degradation of the *as*-triazine ring.

Acetylene groups have recently been used to chain extend and cross-link oligomeric phenylenes,[3] imides,[4] phenylquinoxalines,[5] and ether ketone sulfones;[6] to rigidize and/or cross-link polyphenylquinoxalines[7] and polyimides;[8] and to serve as reactive plasticizers for polysulfones[9] and polyphenylquinoxalines.[10] Acetylene-terminated phenylquinoxaline oligomers were recently prepared by the reaction of 4-(4-ethynylphenoxy)benzil with *o*-diamino end-capped phenylquinoxaline oligomers and subsequently thermally polymerized.[11] Since the synthesis of polyphenylquinoxalines and polyphenyl-*as*-triazines employs a common monomer, the bis(1,2-dicarbonyl) compound, 4-(4-ethynylphenoxy)benzil, was used to prepare acetylene-terminated phenyl-*as*-triazine oligomers as described herein. This work was performed in an attempt to obtain polymers containing the phenyl-*as*-triazine ring with improved processability and structural integrity at temperatures as high as 533 K.

Experimental Section

Monomers and Reactants. The monomers and reactants for model compound work listed in Table I were prepared through known procedures or a slight modification thereof.

Perfluorobutyramidrazone. This compound was prepared by bubbling perfluorobutyronitrile slowly through a solution of 97% hydrazine in 2-propanol at 278 K (5 °C). After complete addition, the solution was stirred at ambient temperature for 2 h followed by removing the 2-propanol under vacuum at <303 K (30 °C). A white crystalline solid formed which was isolated, washed with cold 2-propanol, and recrystallized from cyclohexane to yield white platelets of perfluorobutyramidrazone, mp 342–342.5 K (69.0–69.5 °C).

2-Pyridylamidrazone. 2-Cyanopyridine was reacted with hydrazine in ethanol following a known procedure[13] to provide a pale yellow solid which was recrystallized from benzene to yield white needles, mp 367–368 K (94–95 °C).

Oxalamidrazone. According to a known procedure,[14] dicyanogen was bubbled through a cold solution of hydrazine in ethanol to provide pale yellow crystals, mp 451–452 K (178–179 °C) dec [introduced into preheated oil bath at 433 K (160 °C)].

Perfluoroadipamidrazone. The diamidrazone was prepared as previously reported[15] from the reaction of perfluoroadiponitrile with hydrazine in 2-propanol. White crystals, mp 456–457 K (183–184 °C) dec [introduced into pretreated oil bath at 443 K (170 °C)] were obtained after recrystallization from a mixture of 2-propanol and water.

2,6-Pyridinediyl Diamidrazone. 2,6-Dicyanopyridine was reacted with hydrazine in ethanol according to a known procedure[16] to provide a yellow solid. The crude 2,6-pyridinediyldiamidrazone was recrystallized by adding it to water preheated to 353 K (80 °C) to effect dissolution. Prolonged heating and higher temperatures resulted in partial degradation of the diamidrazone. Pale yellow needles, mp

Table I
Melting Points of Monomers and Reactants

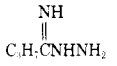
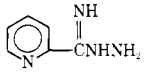
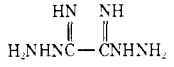
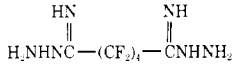
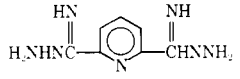
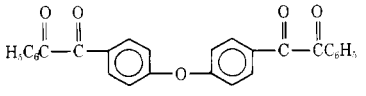
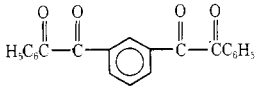
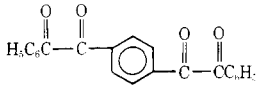
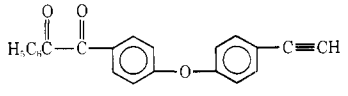
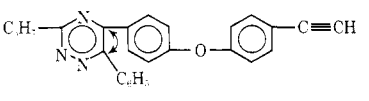
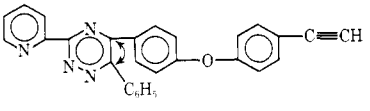
Compd	Mp, K (°C)	Lit. mp, K (°C) [ref]
	342–342.5 (69.0–69.5)	342.5–343 (69.5–70) [12]
	367–368 (94–95)	368–369 (95–96) [13]
	451–452 dec (178–179)	452–453 dec (179–180) [14]
	456–457 dec (183–184)	456–457 dec (183–184) [15]
	502–503 dec (229–230)	503–504 dec (230–231) [16]
	380–381 (107–108)	379.4–380.4 (106.4–107.4) [17]
	372–373 (99–100)	371–372.5 (98–99.5) [18]
	399–398 (124–125)	398–399 (125–126) [19]
	Yellow oil	Yellow oil [20]

Table II
Characterization of Model Compounds

		
Form	Yellow glass	Yellow solid
Mp, K (°C)	318–325 (45–52)	336–343 (63–70)
Formula	$C_{26}H_{14}F_7N_3O$	$C_{28}H_{18}N_4O$
Mol wt[a] (theoretical)	517 (517)	426 (426)

	% C	% H	% N	% F	% C	% H	% N
Elemental Anal	59.98	2.77	8.36	25.42	78.60	4.29	13.13
(theoretical)	(60.36)	(2.72)	(8.12)	(25.70)	(78.86)	(4.25)	(13.14)

[a] Determined by mass spectroscopy.

502–503 K (229–230 °C) dec [introduced into preheated oil bath at 493 K (220 °C)], were obtained.

4,4′-Oxydibenzil. Following a known procedure,[16] diphenyl ether was reacted with phenylacetyl chloride in the presence of aluminum chloride in methylene chloride to provide the intermediate diketone which was oxidized with selenium dioxide in glacial acetic acid. The crude yellow solid was recrystallized from ethanol to provide yellow crystals, mp 380–381 K (107–108 °C).

1,3- and 1,4-Bis(phenylglyoxalyl)benzene. The two dibenzils were prepared following a procedure similar to that reported for 4,4′-oxydibenzil. The diacid chloride of 1,3- or 1,4-phenylenediacetic acid was reacted with benzene in the presence of aluminum chloride in methylene chloride and the resulting intermediate diketones were oxidized with selenium dioxide in glacial acetic acid. Each dibenzil was recrystallized from ethanol to provide yellow crystals, mp 372–373 K (99–100 °C) for the 1,3 isomer and mp 397–398 K (124–125 °C) for the 1,4 isomer.

4-(4-Ethynylphenoxy)benzil. This compound was prepared by a modification of a known procedure.[20] This involved the addition of an aqueous sodium hydroxide solution to the β-chlorocinnamaldehyde in dioxane rather than the reverse addition previously used. A solution of sodium hydroxide (3.0 g, 75 mmol) in water (50 mL) was added dropwise during 0.5 h to a solution of 4-phenylglyoxalylphenoxy-β-chlorocinnamaldehyde (3.0 g, 7.7 mmol) in dioxane (50 mL) at 288 K (15 °C). After complete addition, the brown reaction mixture was stirred at 299 K (26 °C) for 2 h and then poured into cold water (300 mL). The orange aqueous solution was allowed to stand for 4 h and decanted to leave a residual gum. The gum was dissolved in methylene chloride (100 mL) and the solution was washed three times with water, dried over anhydrous magnesium sulfate, filtered, and concentrated to dryness. The residual yellow gum was dissolved in hot cyclohexane (200 mL) and the solution was treated with charcoal, filtered, and concentrated to yield 4-(4-ethynylphenoxy)benzil (1.8 g, 72% yield) as a yellow oil. Anal. Calcd for $C_{22}H_{14}O_3$: C, 80.97; H, 4.32. Found: C, 80.83; H, 4.29.

Model Compounds. Two model compounds shown in Table II were prepared by the following procedures.

3-Heptafluoropropyl-5-phenyl-6-[4-(4-ethynylphenoxy)-phenyl]-*as*-triazine (and Isomer). A solution of 4-(4-ethynylphenoxy)benzil (0.9790 g, 3.0 mmol) and perfluorobutyramidrazone (0.681 g, 3.0 mmol) in ethanol (20 mL) was stirred at ambient temperatures for 3 days and at the reflux temperature for 3 h. The orange solution was concentrated to provide a residual orange gum which slowly solidified. The glassy orange solid was dissolved in cyclohexane (20 mL) and the solution was treated with charcoal and filtered. The cooled filtrate was concentrated to dryness to provide 3-heptafluoropro-

pyl-5-phenyl-6-[4-(4-ethynylphenoxy)phenyl]-*as*-triazine (and isomer) as a glassy yellow solid (1.3 g, 87% yield). Characterization is given in Table II.

3-(2-Pyridyl)-5-phenyl-6-[4-(4-ethynylphenoxy)phenyl]-*as*-triazine (and Isomer). A solution of 4-(4-ethynylphenoxy)benzil (1.6316 g, 5.0 mmol) and 2-pyridylamidrazone (0.681 g, 5.0 mmol) in ethanol (80 mL) was stirred at ambient temperature for 0.5 h and at the reflux temperature for 0.5 h. The hot orange solution was treated with charcoal and filtered, and the filtrate was concentrated to yield an orange gum. The orange gum was dissolved in benzene (50 mL), and the solution was treated with charcoal, filtered, and concentrated to afford 3-(2-pyridyl)-5-phenyl-6-[4-(4-ethynylphenoxy)phenyl]-*as*-triazine (and isomer) as a yellow solid (1.9 g, 84% yield). The yellow solid was dissolved in cyclohexane (150 mL), and the solution was treated with charcoal and filtered. The cooled filtrate was concentrated to dryness to yield a yellow solid whose characterization is given in Table II.

Polymers. Acetylene-terminated phenyl-*as*-triazine oligomers were prepared by two methods. Method 1 involved the reaction of the diamidrazone (1.0 mmol) with the bisbenzil (0.5 mmol) to provide an amidrazone end-capped phenyl-*as*-triazine oligomer which was subsequently reacted with 4-(4-ethynylphenoxy)benzil (1.0 mmol) to provide an acetylene-terminated phenyl-*as*-triazine oligomer. Method 2 involved the reaction of the diamidrazone (1.0 mmol) with the bisbenzil (0.5 mmol) and 4-(4-ethynylphenoxy)benzil (1.0 mmol) to provide an acetylene end-capped phenyl-*as*-triazine oligomer. The following procedures are representative of those used for oligomer preparations from oxalamidrazone and 2,6-pyridinediyldiamidrazone. With perfluoroadipamidrazone, the initial oligomeric solution in method 1 was stirred at ambient temperature for 3 days followed by stirring at 363 K (90 °C) for 4 h. In method 2, the oligomer solution was stirred at ambient temperature for 3 days and at 363 K (90 °C) for 4 h.

Method 1. A mixture of oxalamidrazone (0.1161 g, 1.0 mmol) and 4,4′-oxydibenzil (0.217 g, 0.5 mmol) in *m*-cresol (5 mL) was stirred at ambient temperature for 4 h to yield a yellow solution which was heated to 363 K (90 °C) for 2 h. A solution of 4-(4-ethynylphenoxy)-benzil (0.326 g, 1.0 mmol) in methylene chloride (5 mL) was added to the cooled oligomeric solution followed by stirring at ambient temperature for 4 h and at 363 K (90 °C) for 2 h. The slightly orange solution was poured into methanol to precipitate a yellow solid which was thoroughly washed with hot methanol and dried at 373 K (100 °C) in vacuo for 2 h.

Method 2. Oxalamidrazone (0.1161 g, 1.0 mmol), 4,4′-oxydibenzil (0.2172 g, 0.5 mmol), and 4-(4-ethynylphenoxy)benzil (0.3263 g, 1.0 mmol) were stirred in a mixture of *m*-cresol (5 mL) and methylene chloride (5 mL) at ambient temperature for 4 h and at 363 K (90 °C) for 2 h. The resulting yellow solution was poured into methanol to precipitate a yellow solid which was thoroughly washed with hot methanol and dried at 373 K (100 °C) in vacuo for 2 h.

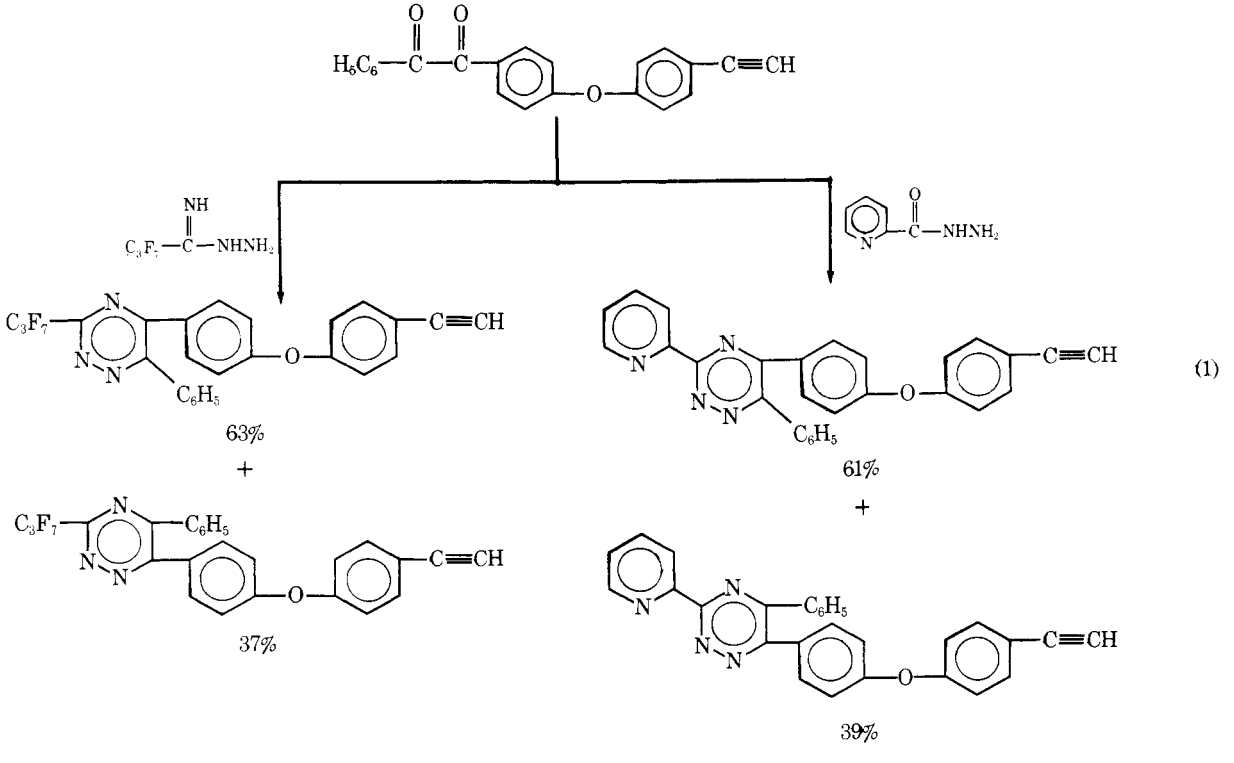
Results and Discussion

Monomers and Reactants. The monomers and reactants listed in Table I were prepared by known procedures as indicated in the Experimental Section. The yield of 4-(4-ethynylphenoxy)benzil was significantly improved from that previously reported[20] (72% vs. 20%) by adding the aqueous sodium hydroxide solution to a dioxane solution of 4-phenylglyoxalylphenoxy-β-chlorocinnamaldehyde and maintaining the temperature <299 K (26 °C). Excess sodium hydroxide and higher temperatures as used in the previously reported synthesis[20] result in excessive cleavage of the α-diketone. Various attempts to induce crystallization of 4-(4-ethynylphenoxy)benzil by trituration and cooling resulted in a yellow gum. This was surprising since 4-(3-ethynylphenoxy)benzil was reported to be a pale yellow solid melting at 352–354 K (79–81 °C).[21]

All monomers were characterized by differential thermal analysis and/or high-pressure liquid chromatography prior to use in polymer formation and were shown to exhibit high purity.

Model Compounds. Two model compounds were prepared from the reaction of 4-(4-ethynylphenoxy)benzil with perfluorobutyramidrazone and 2-pyridylamidrazone as shown in eq 1. The product from each reaction melted over a 7 K range suggesting isomeric products.

High pressure liquid chromatography (HPLC) disclosed two components in each product with the relative amounts indicated in eq 1. Mass spectroscopy confirmed that the two components were isomers. The presence of two isomers in each model compound product was expected due to the anticipated difference in the reactivity of the two carbonyl groups. The model compound with the phenyl group located in the 6 position would be expected to be the predominant isomer in each product based upon a consideration of the relative reactivity of the two carbonyl groups. The carbonyl adjacent to the phenyl group should be the more reactive since the electron



(1)

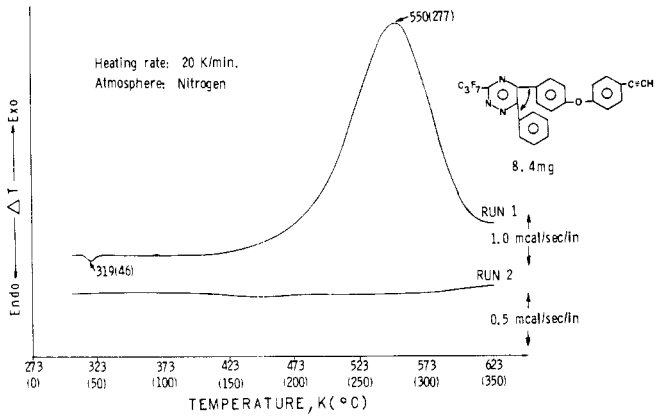


Figure 1. Differential scanning calorimetry of model compound.

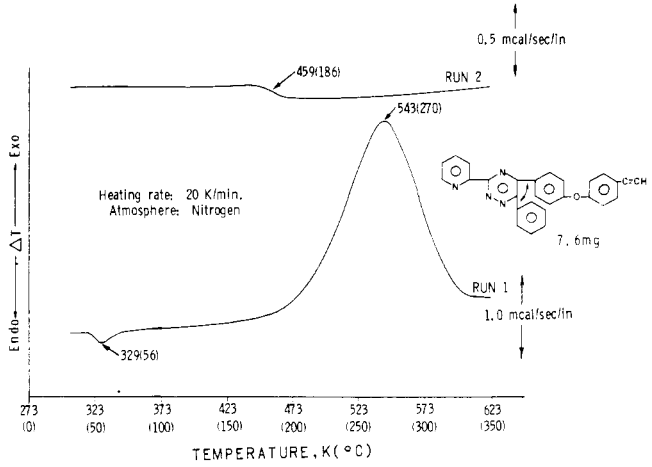
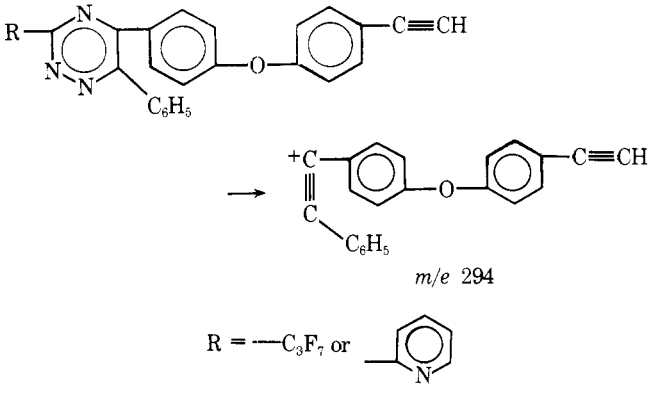


Figure 2. Differential scanning calorimetry of model compound.

density of the other carbonyl would be expected to be higher from contribution of electrons from the ether oxygen.

A preparative separation by HPLC of each product was performed and the two components from each product were analyzed by mass spectroscopy. The fragmentation pattern from electron impact was essentially identical for each of the two components from the two model compound products. The principal fragment from each component had an *m/e* of 294 which corresponded with that expected for cleavage of the *as*-triazine ring.



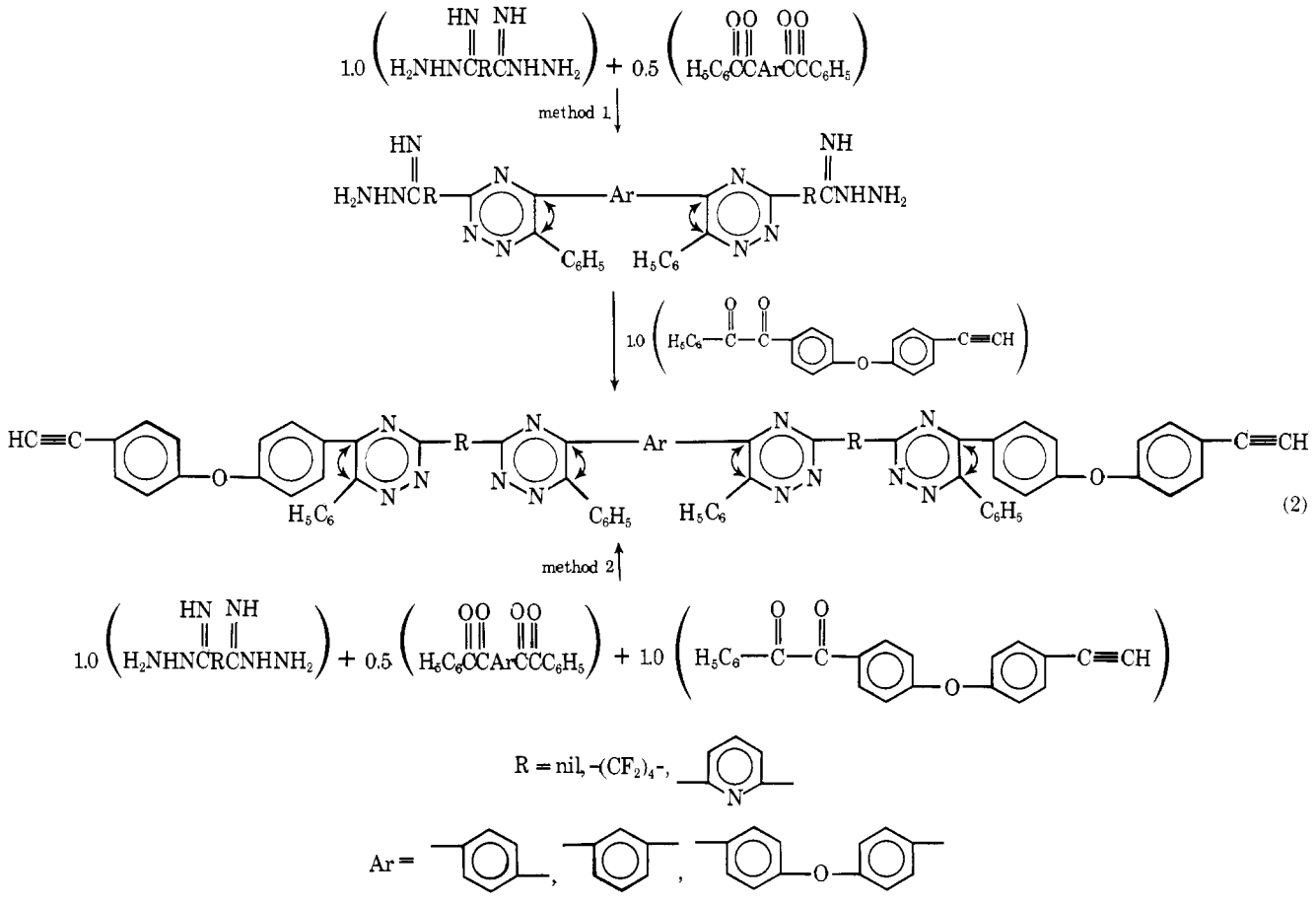
The thermal reaction of an acetylene group is very complex as shown in previous work with acetylene-containing phenylquinoxalines.[20,23] This reaction is even more complex when a mixture of two isomers of an acetylene-containing phenyl-*as*-triazine is thermally reacted. The differential scanning calorimetry (DSC) curves for two acetylene-containing phenyl-*as*-triazine model compounds are shown in Figures 1 and 2. The perfluoropropyl and pyridyl model compounds gave similar DSC curves with melting endotherms peaking at 319 K (46 °C) and 329 K (56 °C) and exotherms peaking at 550 K (277 °C) and 543 K (270 °C), respectively. Upon rerunning each sample after heating to 623 K (350 °C) in nitrogen, the pyridyl model compound sample gave a deflection at ~459 K (186 °C) characteristic of a second-order transition whereas no major thermal transitions were detected for the perfluoropropyl model compound sample.

Using tin as a standard, the heat of reaction (ΔH) was determined for each model compound product at a heating rate of 5, 10, 20, and 50 K/min. The heat of reaction was found to be independent of heating rate which indicated that the thermal reaction of the acetylene group is proceeding faster than the heating rate. The perfluoropropyl and pyridyl model compound gave ΔH of 40.7 ± 1 and 41.4 ± 1 kcal/mol respectively under each of the four heating rates. The reaction of the acetylene group on each model compound should not be influenced by the other end of the molecule except for molecular mobility and therefore was expected to have similar ΔH.

For polymer work, it was of interest to know the minimum temperature for reaction of the acetylene groups, the effect of higher temperature upon the product, and the identity of the major component in the product. Similar to work with an acetylene-containing phenylquinoxaline compound,[20] samples of each of the two model compound products were separately heated for 0.5 h at 468 (195), 523 (250), 568 (295), and 623 K (350 °C) in nitrogen and each soluble product analyzed by HPLC. Full details of this work will be published elsewhere.[22] After heating samples of the perfluoropropyl model compound at each of the temperatures, the products were soluble in chloroform which permitted analysis by HPLC. The chromatogram showed that 55.9% of the perfluoropropyl model compound remained unchanged after 0.5 h at 468 K (195 °C). The remaining 44.1% consisted of two peaks. After 0.5 h at 523 K (250 °C), only 9.0% of the perfluoropropyl model compound remained unchanged with the remainder represented by nine peaks. After 0.5 h at 568 K or 623 K (350 °C), a complex mixture was formed as indicated by numerous peaks and shoulders in the chromatograms. No unreacted perfluoropropyl model compound was detected.

The products from heating samples of the pyridyl model compound at 468 (195) and 523 K (250 °C) were soluble in chloroform whereas the products formed at 568 (295) and 623 K (350 °C) were not completely soluble in chloroform. The chromatogram indicated that 62.1% of the pyridyl model compound remained unchanged after 0.5 h at 468 K (195 °C). The remaining 37.9% consisted of three peaks and a shoulder. After 0.5 h at 523 K (250 °C), 7.8% of the pyridyl model compound remained unchanged with the remainder represented by numerous peaks and shoulders.

Polymers. Acetylene-terminated phenyl-*as*-triazines were prepared by two methods as shown in eq 2. Method 1 involved a two-step process where excess diamidrazone was reacted with the dibenzil in *m*-cresol to provide an amidrazone end-capped phenyl-*as*-triazine oligomer which was subsequently reacted with 4-(4-ethynylphenoxy)benzil in methylene chloride to yield the acetylene-terminated phenyl-*as*-triazine oligomer (ATPT). Method 2 involved the direct synthesis of ATPT by reaction of the diamidrazone, the dibenzil, and 4-(4-ethynylphenoxy)benzil in a mixture of *m*-cresol and methylene chloride. The ATPT listed in Table III were isolated by precipitation in methanol, washed thoroughly in hot methanol, and dried at 373 K (100 °C) in vacuo for 2 h. The stoichiometry for ATPT synthesis was held constant and consisted of 1 mol of diamidrazone, 0.5 mol of dibenzil, and 1.0 mol of 4-(4-ethynylphenoxy)benzil to give ATPT with the



(2)

theoretical molecular weights shown in Table III. Future work is planned to vary the molecular weight of the ATPT and to determine what effect this has on their physical and mechanical properties.

Gel permeation chromatography disclosed that the ATPT prepared by method 2 exhibited a more narrow molecular weight distribution and slightly lower molecular weight than those prepared by method 1. This difference is reflected in the solubility characteristics, polymer melt temperature, and ΔH of the ATPT and the T_g of the thermally cured polymers as discussed in the following paragraphs.

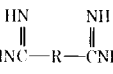
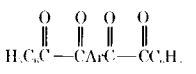
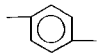
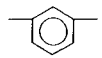
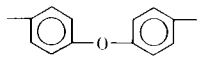
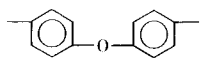
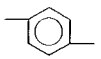
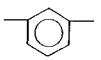
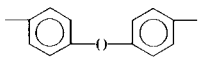
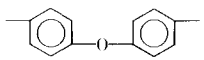
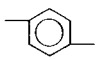
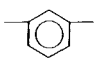
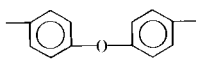
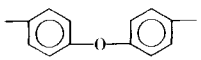
The ATPT from both synthetic methods were soluble at 299 K (26 °C) at 20% solids content (w/v) in chloroform, tetrahydrofuran, dioxane, and *m*-cresol. The ATPT prepared by method 2 exhibited better solubility than those prepared by method 1 as evidenced by more rapid dissolution and better solubility in other solvents such as cyclohexanone. The solubility of the ATPT shown in Table III increased as the diamidrazone portion of the molecule was changed from nil to 2,6-pyridinediyl to octafluorobutylene. The ATPT containing the octafluorobutylene group were readily soluble at 299 K (26 °C) at 20% solids content in acetone.

The heats of reaction for the ATPT shown in Table III prepared by methods 1 and 2 were determined in a manner similar to that for the model compounds using tin as a standard. Since the theoretical and not determined molecular weights of the ATPT were used to calculate the ΔH, the ΔH values are relative and not necessarily real values. As shown in Table III, the ΔH increased as the diamidrazone portion of the ATPT was changed from octafluorobutylene to 2,6-pyridinediyl to nil. This trend was unexpected since the oligomer with the greatest molecular mobility was anticipated to yield the most efficient cross-linking and therefore the highest ΔH. The ATPT prepared by method 2 exhibited higher ΔH than those prepared by method 1 as expected due to a more efficient cure from a more mobile lower molecular weight material.

The T_gs of the thermally cured ATPT were determined by DSC and torsional braid analysis (TBA). Representative DSC curves at a heating rate of 20 K/min of the perfluoroamidrazone-derived ATPT from 4,4′-oxydibenzil via method 2 (PF-4) and its thermally cured polymer are shown in Figure 3. All of the ATPT and their thermally cured polymers exhibited DSC curves similar to that shown in Figure 3. No difference in the general shape of the curve was observed due to the method of oligomer preparation. Obvious differences were observed in the temperatures of the melting endothermic peaks, exothermic peaks, and T_g transitions. The latter two temperatures for all of the ATPT and polymers are reported in Table III. In Figure 3, the endotherm peaking at 412 K (139 °C) is due to melting of the ATPT. The broad exotherm which extends from ~423 (150 °C) to ~593 K (320 °C), peaking at 541 K (268 °C), is undoubtedly due to the thermal reaction of the acetylene groups. The sample was held at 593 K (320 °C) in nitrogen for 0.5 h and then rerun to exhibit a T_g of 478 K (205 °C).

The TBA curves obtained at a heating rate of 3 K/min for the perfluoroadipamidrazone-derived ATPT differed from those of the 2,6-pyridinediyldiamidrazone- or oxalamidrazone-derived ATPT. Since the general shape of the TBA curve for the latter two ATPT systems is similar, the oxalamidrazone-derived ATPT is shown as the representative example. The TBA curves of each material prepared by methods 1 and 2 were very similar. The broad damping peak and change in rigidity in the 173 K (−100 °C) to 283 K (10 °C) range shown in Figure 4 for the perfluoroamidrazone-derived ATPT (PF-3) is due to absorbed water. A damping peak maximizing at 407 K (134 °C) with a corresponding decrease in the relative ri-

Table III
Characterization of Acetylene-Terminated Phenyl-*as*-triazine Oligomers and Polymers

Polymer designation	 R =	 Ar =	Syn method[a]	Calcd av mol wt of oligomer	PMT, K (°C)[b]	DSC, K (°C)[c] Exothermic peak	DSC, K (°C)[c] T_g	TBA, K (°C)[d] Damping peak	TBA, K (°C)[d] T_g	ΔH, kcal/mol
PF-1	$-(CF_2)_4-$		1	1452	427–435 (154–162)	549 (276)	471 (198)			
PF-2			1	1452	423–431 (150–158)	548 (275)	464 (191)			
PF-3			1	1564	419–430 (146–157)	549 (276)	456 (183)	407 (134)	462 (189)	−26.9
PF-4			2	1564	417–427 (144–154)	541 (268)	478 (205)	404 (131)	479 (206)	−46.4
PY-1			1	1204	491–498 (218–225)	546 (273)	562 (289)			
PY-2			1	1204	486–495 (213–222)	545 (272)	548 (275)			
PY-3			1	1296	483–491 (210–218)	545 (272)	533 (260)	471, 533 (198, 260)	542 (269)	−36.7
PY-4			2	1296	474–481 (201–208)	545 (272)	556 (282)	463, 488 (191, 215)	565 (292)	−61.9
OX-1	NIL		1	1050	514–523 (241–250)	530 (257)	590 (217)			
OX-2			1	1050	509–516 (236–243)	529 (256)	581 (308)			
OX-3			1	1141	474–483 (201–210)	530 (257)	577 (304)	489, 563 (216, 290)	593 (320)	−49.8
OX-4			2	1141	468–478 (195–205)	530 (257)	603 (330)	458, 485 (185, 212)	Not detected	−73.0

[a] See Experimental Section. [b] Determined on Fisher-Johns melting point apparatus under slight spatula pressure. [c] Heating rate of 20 K/min, T_g taken at inflection point of ΔT vs. temperature curve, all samples were cured at 593 K (320 °C) for 0.5 h, N_2, prior to T_g determination. [d] Heating rate of 3 K/min, T_g taken at maximum damping peak.

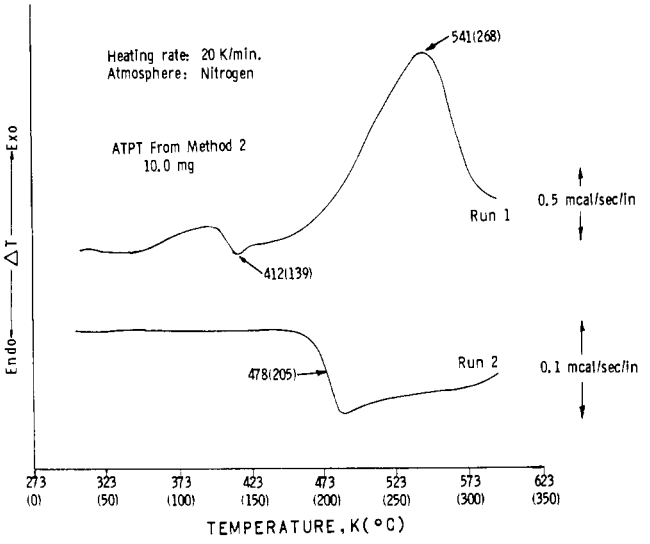


Figure 3. Differential scanning calorimetry of the perfluoroamidrazone-derived ATPT from 4,4′-oxydibenzil via method 2.

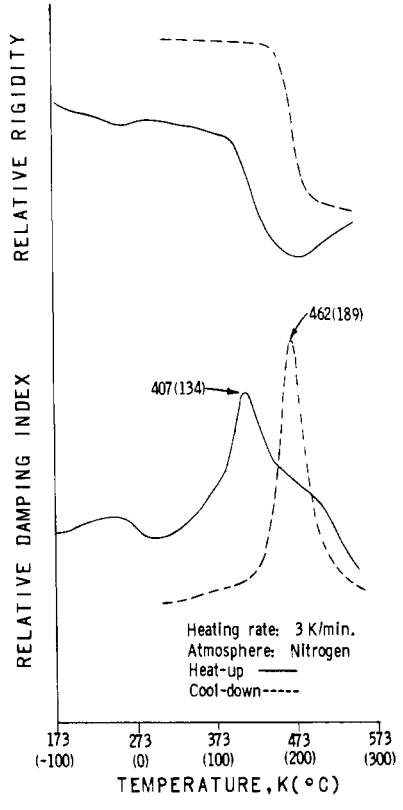


Figure 4. Torsional braid analysis of perfluoroamidrazone-derived ATPT from 4,4′-oxydibenzil via method 1.

gidity is due to the sample melting. As shown by DSC work, the exothermic cure begins at ~ 423 K (150 °C) which is shown as the shoulder on the damping peak of the TBA curve. As the sample cures, the relative rigidity increases. The sample was held at 548 K (275 °C) for 0.5 h in nitrogen and the cool-down curve was obtained. A maximum damping peak at 462 K (189 °C) corresponding to a drastic change in the relative rigidity was taken as the T_g.

The oxalamidrazone-derived ATPT (OX-3) provided a different shaped TBA curve as shown in Figure 5. A broad damping peak and relative rigidity change also occurred in the 173 K (−100 °C) to 283 K (10 °C) range due to the presence of absorbed water. The intense damping peak maximizing at

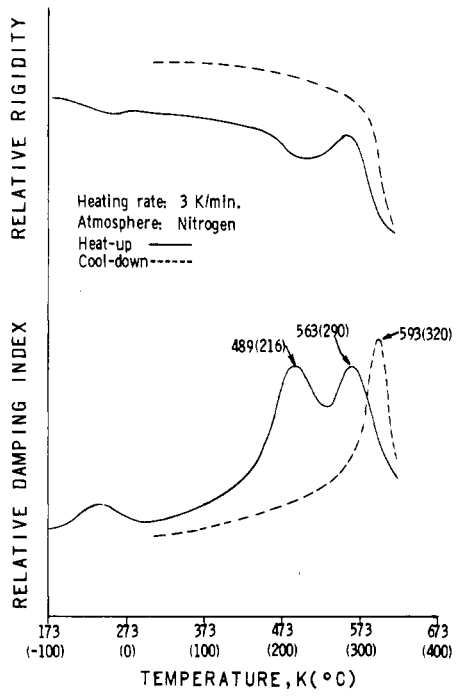


Figure 5. Torsional braid analysis of oxalamidrazone-derived ATPT from 4,4′-oxydibenzil via method 1.

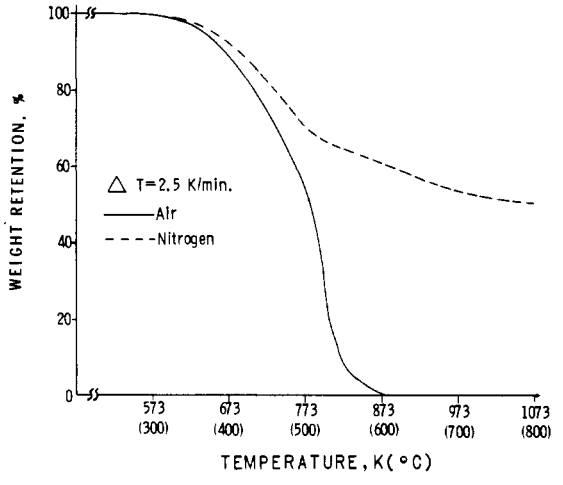


Figure 6. Thermogravimetric analysis of 573 K (300 °C) cured perfluoroamidrazone-derived ATPT from 4,4′-oxydibenzil via method 1.

489 K (216 °C) accompanied by a decrease in the relative rigidity is apparently due to the sample melting. The next damping maximum at 563 K (290 °C) is the T_g. After heating to 623 K (350 °C) in nitrogen, the cool-down curve shows a sharp damping maximum at 593 K (320 °C) with a corresponding sharp change in relative rigidity indicating that the T_g has increased due to further cure at the higher temperature.

In order to obtain comparative T_g values, each ATPT in Table III was cured at 593 K (320 °C) for 0.5 h in nitrogen prior to the T_g determination by DSC. The thermally cured ATPT prepared by method 2 exhibited higher T_gs than those prepared by method 1 apparently due to more molecular mobility resulting in a more efficient cure. In addition, as the flexibility of the diamidrazone portion of the molecule decreased going from octafluorobutylene to 2,6-pyridinediyl to nil, the T_g increased as expected. Within a specific group of polymers where the diamidrazone portion of the molecule

Chart I

Test condition	Flexural st, MPa (Ksi)	Modulus, GPa (psi × 10^6)	Interlaminar shear st, MPa (Ksi)
RT	1386 (201)	135.1 (19.6)	83.4 (12.1)
505 K (232 °C)	1062 (154)	120.0 (17.4)	60.0 (8.7)
533 K (260 °C)	834 (121)	111.7 (16.2)	36.5 (5.3)
533 K after 100 h at 533 K			38.6 (5.6)
533 K after 300 h at 533 K			46.2 (6.7)

remained the same and the bisbenzil portion was changed from *p,p'*-oxydiphenylene to *m*-phenylene to *p*-phenylene, the T_g increased as expected as the flexibility of the molecule decreased.

The thermal stability of various ATPT which were cured for 0.5 h at 573 K (300 °C) in nitrogen was determined by thermogravimetric analysis (TGA) at a heating rate of 2.5 K/min. A representative TGA curve is shown in Figure 6. All the TGA curves obtained in air or nitrogen were essentially the same with the initial weight loss in air commencing at ~603 K (330 °C) with 20% weight loss occurring at 713 K (440 °C). In nitrogen, initial weight loss also began at ~603 K (330 °C) with 20% weight loss occurring at ~733 K (460 °C) and ~50% residue remaining at 1073 K (800 °C).

Preliminary Adhesive Properties. The ATPT from the reaction of oxalamidrazone, 4,4'-oxydibenzil, and 4-(4-ethynylphoxy)benzil prepared by method 2 on a 0.05-mol scale in *m*-cresol at 20% solids content underwent preliminary adhesive evaluation. The ATPT was precipitated from the *m*-cresol solution by quenching in methanol followed by washing thoroughly in hot methanol and drying at 373 K (100 °C) in vacuo for 2 h. The yellow powder [PMT = 466–477 K (193–204 °C)] was dissolved in chloroform (~25% solids content) and this solution was used to prepare an unformulated tape (112 E-glass, A1100 finish, 11–13-mils thick, <0.1% volatiles). Tensile shear specimens using titanium (6A1-4V) adherend having a phosphate fluoride surface treatment and primed with a 5% chloroform solution of the ATPT were fabricated. Curing was accomplished by introducing the assembled panels into a preheated press at 505 K (232 °C) and holding under contact pressure for ~1 min. The pressure was increased to 0.69 MPa (100 psi) and the temperature was increased to 533 K (260 °C), held there under 0.69 MPa (100 psi) for 1 h, and cooled under pressure. The following tensile shear strengths were obtained and are averages of three specimens: 33.5 MPa (4860 psi) at 299 K (26 °C) (cohesive failure), 6.27 MPa (910 psi) at 533 K (260 °C) (mixed failure), and 8.69 MPa (1260 psi) at 533 K (260 °C) after 300 h at 533 K (260 °C) in air (mixed failure but predominantly adhesive). The higher strengths at 533 K (260 °C) after aging are attributed to a postcure effect. The ATPT exhibited excellent flow during fabrication. However, the flash was brittle. Additional work must be done to determine the potential of ATPT as adhesives.

Preliminary Composite Properties. The same ATPT used in adhesive work also underwent preliminary laminate evaluation. Drum-wound Hercules HT-S graphite filament reinforcement was brush coated with a solution of ATPT in a mixture of chloroform and sym-tetrachloroethane (25% solids content). The prepreg was air dried under lamps overnight and then in a forced-air oven at 373 K (100 °C) for ~1 h. Unidirectional laminates [7.6 cm × 17.8 cm × 0.15 or 0.30 cm (3 in. × 7 in. × 0.060 or 0.120 in.)] were fabricated in a mold by introducing the assembly into a preheated press at 505 K (232 °C) and holding under contact pressure for ~2 min. The pressure was increased to 13.8 MPa (200 psi) and the temperature was increased to 533 K (260 °C), held there under 13.8 MPa for 3 h, and cooled under pressure. The following strengths were obtained and represent averages of three specimens (Chart I). The higher interlaminar shear strengths at 533 K after aging are attributed to a postcure effect.

Conclusions

Acetylene-terminated phenyl-*as*-triazine oligomers exhibited good solubility, relatively low polymer melt temperatures, and were thermally cured without volatile evolution to yield resinous materials with high T_g. Model compound work demonstrated that the acetylenic curing reaction provided a complex mixture of products. Preliminary adhesive and composite evaluation provided encouraging results.

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References and Notes

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