Macromolecules **1987,** *20,* 726-729

(br t), 7.45 (br s), 6.96 (q), 4.53 (t), 4.29 (t), 4.19 (t), 4.05 (t), 3.92 (d), 2.29 (br m), 1.75 (br t), 1.61 (br t), 1.28 (br s). Anal. Calcd for $C_{26}H_{35}NO_6$ (values for a hypothetical copolymer repeat unit): C, 68.25; H, 7.71; N, 3.06. Found: C, 68.00; H, 7.72; N, 3.26.

No. 2. Yield 85%; mp ≈130–140 °C; MW 22 000; IR (KBr) 2217, 1731, 1716 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.14 (s), 7.80 (br q), 7.44 (br s), 6.96 (q), 4.53 (br s), 4.29 (t), 4.19 (t), 4.05 (t), 3.92 (s), 2.28 (br m), 1.75 (br t), 1.61 (br t), 1.28 (br s). Anal. Calcd for $C_{26}H_{35}NO_6$ (values for a hypothetical copolymer repeat unit): C, 68.25; H, 7.71; N, 3.06. Found: C, 67.92; H, 7.77; N, 3.06.

No. 3. Yield 91%; mp ≈140–220 °C; MW 64 000; IR (KBr) 2219, 1730, 1714 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.14 (s), 7.80 (br d), 7.44 (br s), 6.96 (q), 4.53 (br t), 4.29 (br t), 4.19 (t), 4.05 (t), 3.92 (s), 2.29 (br m), 1.75 (br t), 1.61 (br t), 1.28 (br s). Anal. Calcd for $C_{26}H_{35}NO_6$ (values for a hypothetical copolymer repeat unit): C, 68.25; 7.71; N, 3.06. Found: C, 68.11; H, 7.81; N, 3.07.

No. 4. Yield 100%; mp ≈190 °C; IR (KBr) 2217, 1714 cm^{-1}; Anal. Calcd for $C_{14}H_{13}NO_4$ (values for the homopolymer repeat unit): C, 64.86; H, 5.05; N, 5.40. Found: C, 64.98; H, 5.65; N, 4.93.

No. 5. Yield 91%; mp (dec) 240 °C; IR (KBr) 2218, 1731 cm^{-1}. Anal. Calcd for $C_{40}H_{48}N_2O_{10}$ (values for a hypothetical copolymer repeat unit): C, 67.02; H, 6.75; N, 3.91. Found: C, 66.89; H, 6.96; N, 3.67.

No. 6. Yield 100%; mp (dec) ≈300–340 °C, IR (KBr) 2217, 1712 cm^{-1}.

No. 7. Yield 80%; mp (dec) ≈250 °C; IR (KBr) 2217, 1726 cm^{-1}; Anal. Calcd for $C_{63}H_{79}N_3O_{14}$ (values for a hypothetical copolymer repeat unit): C, 68.64; H, 7.22; N, 3.81. Found: C, 68.23; H, 6.88; N, 3.64.

No. 8. Yield 87%; mp ≈140–160 °C; MW 34 000; IR (KBr) 2217, 1731, 1715 cm^{-1}. Anal. Calcd for $C_{26}H_{35}NO_6$ (values for a hypothetical copolymer repeat unit): C, 68.25; H, 7.71; N, 3.06. Found: C, 68.02; H, 7.57; N, 3.04.

No. 9. Yield 93%; mp ≈180–185 °C; IR (KBr) 2217, 1729 cm^{-1}. Anal. Calcd for $C_{63.4}H_{69.7}N_{3.67}O_{16.7}$ (values for a hypothetical copolymer repeat unit): C, 66.21; H, 6.11; N, 4.47. Found: C, 65.41; H, 6.17; N, 4.29.

Acknowledgment. This work was generously supported by the Eastman Kodak Co.

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Novel Polymerization Reaction: Double Cycloaddition of Sydnone and Bismaleimide

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ABSTRACT: A novel polymerization reaction of mesoionic sydnone and bismaleimide is described. This polymerization is based on the double 1,3-cycloaddition of sydnone to two maleimide functions to form carbon dioxide and 1,7-diazabicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylic acid diimide (8), which are the recurring units of the polymer chain. A new class of polyimides has been synthesized by this reaction. These polyimides have good thermal stability and solubility.

Introduction

Since the first synthesis of sydnone in 1935 the chemistry of mesoionic heterocyclic compounds has been extensively explored.[1] However, despite the high reactivity of some of its members, the application of mesoionic compounds in the synthesis of macromolecules is extremely limited. Stille and Bedford[2] reported the reaction of disydnone with diene or diyne to form poly(pyrazoline) and poly(pyrazole), respectively, of low to moderate molecular weights. Rigby and Stark[3] described the reaction of some reactive olefins such as bismaleimide with tautomer of 1,3-oxazol-5-one, which is mesoionic 1,3-oxazolium-5-olate, to form insoluble materials. These materials are believed to be polyimides containing 7-azabicyclo[2.2.1]heptane units according to reaction of 1,3-oxazol-5-one and maleimide.[4]

It is now found that the double cycloaddition of sydnone to an equimolar amount of bismaleimide forms a new class of polyimides with a polycyclic structure and usually of high molecular weights. These polyimides have good thermal stability and are soluble in many organic solvents.

Results and Discussions

The 1,3-dipolar cycloaddition reaction of mesoionic sydnone (1) to olefinic double bonds is known to form initially an unstable 1:1 primary adduct, which eliminates carbon dioxide, followed either by 1,3-proton shift to become a Δ^2-pyrazoline or by further elimination of a neutral molecule to form a pyrazole derivative as the final stable products.[5] Only in the reaction of 3-phenylsydnone and acenaphthylene, in addition to the normal product pyrazoline, is a bis adduct formed in low yield.[6] This bis adduct is the result of double cycloaddition of sydnone to two molecules of the olefin after elimination of carbon dioxide. Similarly, in the reaction of sydnone with cyclooctadiene or butadienes, such double cycloaddition occurs intramolecularly to afford low to moderate yield of bis adducts.[7]

It is found that the reaction of 3-phenylsydnone (**1a**) and *N*-phenylmaleimide affords exclusively two isomeric bis adducts, 7-phenyl-1,7-diazabicyclo[2.2.1]heptane-2,3-*exo*-5,6-*exo*-tetracarboxylic acid bis(phenylimide) (**4**) and the corresponding -2,3-*endo*-5,6-*exo*- isomer **5** in practically quantitative yield.[8] Because of the high reactivity of maleimide as a dipolarophile toward azomethine–imine dipoles, such as intermediate **3**, the reaction of the latter with *N*-phenylmaleimide is much faster than its intramolecular rearrangement to the energetically unfavorable pyrazoline **6**, because **6** contains a highly strained double bond. Therefore, in this reaction, the products are exclusively **4** and **5** in 87:13 ratio when the reaction is carried out at 95 °C.

This bifunctional character of sydnone toward maleimide allows its reaction with bismaleimide to form polyimide. Such polymerization is demonstrated by the re-

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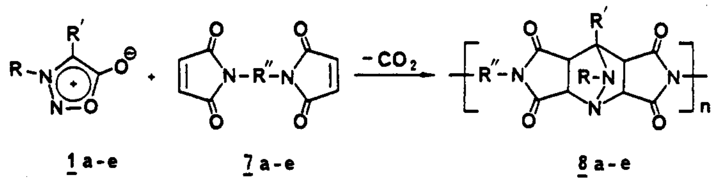
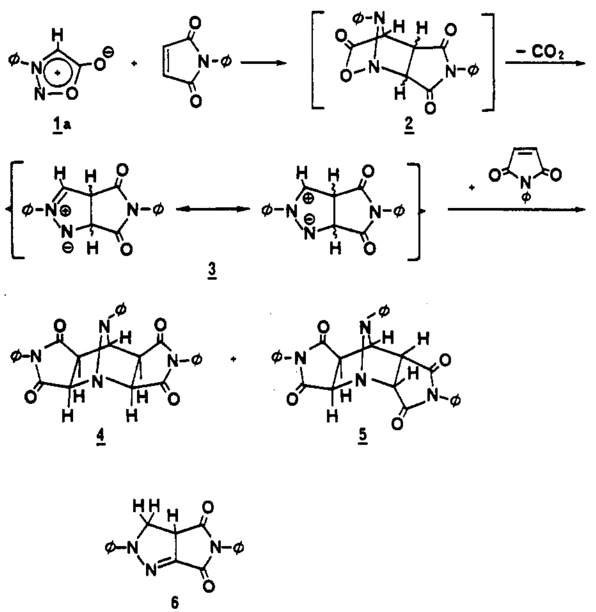
Table I
Reactions of Sydnone and Bismaleimide



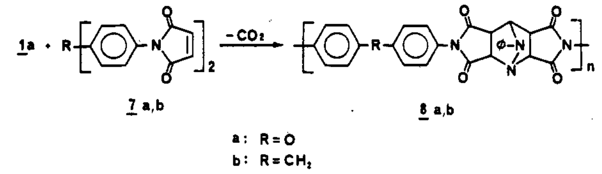
reactn	R	R′	R″	temp, °C (time, h)	solvent[a]	$\eta_{0.5}$(solvent[a])
a	C_6H_5	H	p-$C_6H_4OC_6H_4$-p	95 (24) + 115 (3.5)	A	1.47 (B)
b	C_6H_5	H	p-$C_6H_4CH_2C_6H_4$-p	95 (20) + 115 (4)	A	0.83 (D)
c	C_6H_5	H	CH_2CH_2	95 (20) + 115 (4)	A	0.25 (E)
d	n-C_3H_7	C_2H_5	p-$C_6H_4CH_2C_6H_4$-p	90 (18) + 105 (7)	B	0.91 (B)
e	C_6H_5	C_6H_5	p-$C_6H_4CH_2C_6H_4$-p	115 (26)	C	1.93 (B)

[a] A, tetramethylene sulfone; B, dimethylformamide; C, mixture of dimethylformamide and glacial acetic acid, 9:1 (v/v); D, *m*-cresol; E, 1-methyl-2-pyrrolidinone.

Scheme I



Scheme II



action of 3-phenylsydnone (**1a**) and an aromatic bismaleimide such as 1,1′-(oxydi-4,1-phenylene)bismaleimide (**7a**), or 1,1′-(methylenedi-4,1-phenylene)bismaleimide (**7b**) at 95 °C to generate carbon dioxide and to afford polyimide **8a** or **8b**, respectively.

The resulting polyimides **8a** and **8b** generally have high viscosity, which is a dependent of reaction time and temperature of the polymerization reaction. In the reaction of **1a** and **7a** at 95 °C in tetramethylene sulfone (TMS), within the range 21–28 h, the plot of reaction time against $\eta_{0.5}$ is close to a straight line as shown in Figure 1. Polyimide **8a** of high viscosity ($\eta_{0.5}$ = 1.4) can be prepared by carrying out the polymerization first at 95 °C and then further at higher temperature as indicated in Table I.

The infrared absorptions of **8a**, from 1100 cm^{-1} up, are very similar to and almost superimposing with those of the model compounds **4** and **5**. The ^1H NMR spectrum of **8a**, despite its broad signals, displays the same pattern as that of the exo,exo bis adduct **4**.[8] The bridge head proton (H4) of the diazabicyclo[2.2.1] heptane rings in **8a** appears as a singlet at δ 5.7. Since there is no coupling between H4 and its two neighboring protons H3 and H5 of the bicyclic ring, both H3 and H5 must be endoprotons[9] and therefore, the two imide rings of the bicyclic diimide unit must both have exo configuration. Protons H3 and H5 appear as a doublet at δ 3.8 due to their coupling with H2 and H6, respectively. Similarly, H2 and H6 also appear as a doublet at δ 4.8. This pattern of the protons of the 1,7-diazabicyclo[2.2.1]heptane unit in **8a** is the same as that of the corresponding protons of the exo,exo bis adduct **4** but is different from that of the endo,exo isomer **5**. In the endo,exo isomer, the bridge head proton is split into a doublet due to its coupling with one of the neighboring protons which is in the exo position.[8] On the basis of these spectral data the diimide units in the polymer chain are believed to have mainly exo,exo configuration. However, because of the broad NMR signals the possibility of the presence of a low percentage of *endo,exo*-diimide units in the polymer cannot be excluded.

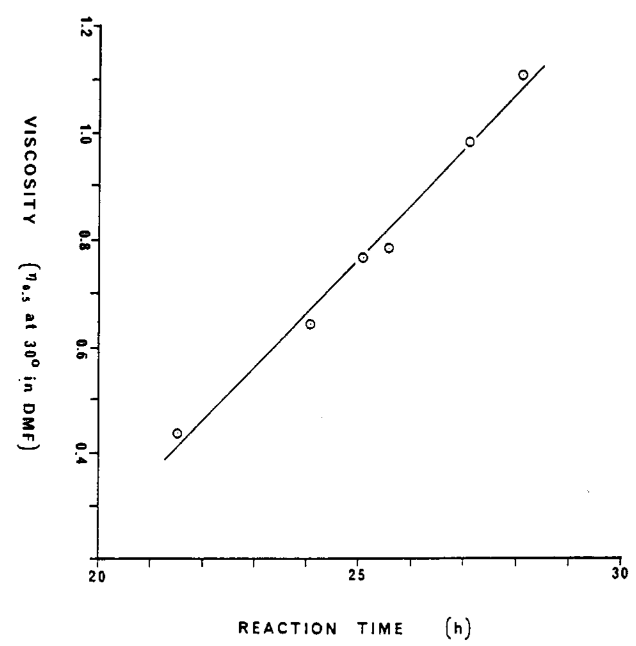
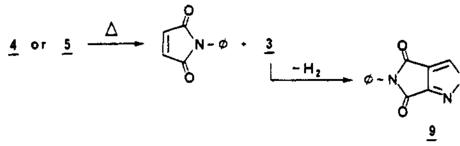


Figure 1. Plot of reaction time vs. viscosity of polyimide **8a** prepared by the reaction of **1a** and **7a** in TMS at 95 °C.

Polyimides **8a** and **8b** are stable in air and start to decompose above 345 °C. It is believed that the decomposition is caused by the cycloreversion of the diazabicyclo[2.2.1]heptane rings in the polymer as demonstrated in the pyrolysis of the model bis adducts **4** and **5**. Both **4** and

Scheme III



5 undergo 1,3-cycloreversion at 310 °C to generate *N*-phenylmaleimide and the cyclic azomethine–imine **3**; the latter further eliminates a molecule of hydrogen to form a stable pyrazole derivative **9**.[10]

Polyimides **8a** and **8b** do not melt or show glass transition up to the temperature of decomposition. Only **8c**, an aliphatic polyimide prepared from 3-phenylsydnone and 1,1′-ethylenebismaleimide (**7c**) demonstrated by differential scanning calorimeter a melting point at 330 °C immediately before its decomposition.

Both **8a** and **8b** are soluble in several types of organic solvents, such as dimethylformamide, dimethylacetamide, 1-methyl-2-pyrrolidinone, tetramethylene sulfone, dimethyl sulfoxide, phenol, *m*-cresol, aniline, trifluoroacetic acid, and dichloroacetic acid. Flexible transparent films of **8a** and **8b** can be cast from a solution of dimethylformamide or trifluoroacetic acid. A film of **8a** of low viscosity ($\eta_{0.5}$ = 0.78) has a tensile strength above 9000 psi, elongation over 10%, and a tensile modulus of around 270 000 psi.

The double 1,3-cycloaddition of mesoionic sydnone to bismaleimide to form carbon dioxide and polyimide with recurring units of bisimide of substituted 1,7-diazabicyclo[2.2.1]heptane-2,3,5,6-tetracarboxylic acid (**8**) appears to be a general reaction.[11] Besides the reactions of 3-phenylsydnone with aromatic and aliphatic bismaleimides discussed above, other sydnones, such as **1d** and **1e**, also react with bismaleimide **7b** to form polyimides **8d** and **8e**, respectively. The results and conditions of the polymerization reaction are summarized in Table I.

Model reactions of this polymerization, such as the reaction of **1a** with *N*-phenyl- or *N*-methylmaleimide and **1d** or **1e** with *N*-phenylmaleimide, have already been discussed in a communication.[8]

Experimental Section

Materials. Sydnones: **3-Phenylsydnone (1a)** was prepared according to an *Organic Synthesis* procedure.[12] 3-*n*-Propyl-4-ethylsyndone (**1d**) was prepared according to a reported procedure for 4-isobutyl-3-methylsydnone.[13] **1d** was obtained as a somewhat unstable light yellow oil: bp 128–130 °C (0.02 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.05 (t, *J* = 7.2 Hz, CH_3), 1.23 (t, *J* = 7.0 Hz, CH_3), 2.0 (m, *J* = 7.0 Hz, CH_2), 2.7 (q, *J* = 7.2 Hz, CH_2), 4.2 (t, *J* = 7.0 Hz, NCH_2). A freshly distilled sample was reacted with excess *N*-phenylmaleimide according to the procedure for the preparation of **4** and **5** to form carbon dioxide and a solid bis adduct in 81% isolated yield;[8] this solid adduct melts at 226.5–227.5 °C. Anal. Calcd for $C_{26}H_{26}N_4O_4$: C, 68.10; H, 5.72; N, 12.22. Found: C, 68.10; H, 5.60; N, 12.23. 3,4-Diphenylsydnone (**1e**) was prepared according to the procedure reported by Baker, Ollis, and Poole.[14]

Bismaleimides: **1,1′-(Oxydi-4,1-phenylene)bismaleimide (7a)**. The bismaleamic acid obtained from the reaction of di(4-aminophenyl) ether and excess maleic anhydride in chloroform at room temperature was cyclodehydrated by acetic anhydride in the presence of sodium acetate according to the procedure of Kovacic and Hein.[15] The crude product was recrystallized from a mixture of dichloromethane and ether and then from hot glacial acetic acid: mp 185–186.5 °C. 1,1′-(Methylenedi-4,1-phenylene)bismaleimide (**7b**) was obtained from Aldrich Chemical Co. and was recrystallized as described for **7a**, mp 161.5–162.5 °C. 1,1′-Ethylenebismaleimide (**7c**) was also prepared according to the procedure by Kovacic and Hein.[15]

Solvents. Dimethylformamide (DMF) was purified by drying HPLC grade DMF with Linde Molecular sieves 4A. The dry solvent was fractionated under 30 mmHg. The constant boiling fraction (65 °C) was used immediately after distillation. A mixture of HPLC grade DMF and 10% (v) glacial acetic acid can also be used in lieu of pure DMF. Tetramethylene sulfone (TMS) was also purified by the same method as described for DMF, except the solvent was stirred with molecular sieves at 50 °C and fractionated at 1 mmHg.

Procedure for the Polymerization. A solution of sydnone (20.0 mmol) and bismaleimide (20.0 mmol) in 90 mL of solvent was stirred under dry nitrogen and at the temperature given in Table I. Carbon dioxide started to generate at around 80 °C and was vented through a microbubbler. After the reaction the hot viscous solution was poured slowly into 5 L of cold water. The polyimide thus solidified was washed with slowly running water and then with several batches of acetone. The polymer was dried at 140 °C (0.1 mmHg). A 90–96% yield of white to light cream polyimide was obtained. Viscosity ($\eta_{0.5}$) of the polymer was determined at 30 °C in the solvent indicated in Table I.

Polyimide 8a. IR (KBr) 3080, 1780, 1720, 1597, 1497, 1375, 1240, 1195 cm^{-1}; ^{1}H NMR (DMF-d_7) broad signals δ 3.8 (d, $J_{3,2}$, $J_{5,6}$ = 6 Hz, H3, 5), 4.8 (d, $J_{2,3}$, $J_{6,5}$ = 6 Hz, H2,6), 5.7 (s, H4), 6.7–7.4 (m, aromatic). Anal. Calcd for $C_{27}H_{18}N_4O_5$: C, 67.77; H, 3.79; N, 11.71. Found: C, 66.83; H, 3.83; N, 11.48.

Polyimide 8b. IR (KBr) 3040, 1785, 1720, 1598, 1510, 1495, 1370, 1300, 1190 cm^{-1}; ^{1}H NMR (DMF-d_7) broad signals δ 3.7 (d, $J_{3,2}$, $J_{5,6}$ = 6 Hz, H3,5), 4.1 (s, CH_2), 4.7 (d, $J_{2,3}$, $J_{6,5}$ = 6 Hz, H2,6), 5.7 (s, H4), 6.6–7.3 (m, aromatic). Anal. Calcd for $C_{28}H_{20}N_4O_4$: C, 70.57; H, 4.23; N, 11.76. Found: C, 69.83; H, 4.26; N, 11.58.

7-Phenyl-1,7-diazabicyclo[2.2.1]heptane-2,3-*exo*-5,6-*exo*-tetracarboxylic Acid Bis(phenylimide) (4) and 7-Phenyl-1,7-diazabicyclo[2.2.1]heptane-2,3-*endo*-5,6-*exo*-tetracarboxylic Acid Bis(phenylimide) (5). Sydnone **1a** (1.62 g, 10 mmol) and *N*-phenylmaleimide (5.19 g, 30 mmol) in dry toluene (30 mL) were stirred under nitrogen at 95 °C for 6 h to give carbon dioxide and colorless precipitates. The reaction mixture was cooled in an ice bath. The crystalline product was washed with cold toluene and dried at 125 °C (0.1 mmHg). A total of 3.81 g of **4** was obtained: mp 286–287 °C. To the combined mother liquor and washings was added hexane slowly, and 0.19 g more of **4** precipitated on standing, mp: 285–286 °C. The toluene/hexane mother liquor was evaporated, the residue was stirred with ether, and 0.60 g of light yellow crystalline **5** precipitated, which sometimes contained trace of **4**: mp 271–272.5 °C. Total yield of **4** and **5** was 4.60 g (99%). The ratio **4**:**5** was 87:13. TLC (silica gel, toluene–ethyl acetate as eluting solvents) indicated that the original reaction mixture contained no other detectable product besides **4**, **5**, and the excess *N*-phenylmaleimide. Analytical and spectral data of both **4** and **5** have been given in a previous communication.[8]

2,5-Diphenylpyrrolo[3,4-*c*]pyrazol-(2*H*,5*H*)-4,6-dione (9). Bis adduct **4** or mixture of **4** and **5** (0.929 g, 2.0 mmol) was placed in a distillation flask, which was connected to a short-path air-cooled bridge and a receiver cooled by ice. The pressure of the system was reduced to 0.04 mmHg before the distillation flask was immersed into a 310 °C oil bath. As the bis adduct decomposed 0.32 g (95%) of *N*-phenylmaleimide was condensed in and near the receiver. Another fraction of distillate, a brown solid, condensed just above the distillation flask. It was recrystallized first from toluene and then from a mixture of DMF and chloroform to give 0.40 g (70%) of **9** as almost colorless fine needles: mp 240–241 °C. The analytical and spectral data of 9 have been given in a previous report.[10]

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Aromatic Azomethine Polymers and Fibers[1]

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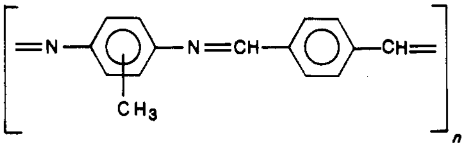
ABSTRACT: The synthesis of a variety of fusible aromatic poly(azomethines) by solution and melt methods is described. The aromatic amine–aldehyde reaction is very rapid, and end-capping is necessary to control molecular weight and restrain polymerization during melt processing. A useful range of melting or softening points (200–350 °C) was attained by ring substitution, copolymerization, and/or introduction of limited chain flexibility. Many of the poly(azomethines) yielded liquid crystalline melts, which were readily spun into oriented, high-tenacity, high-modulus fibers. These fibers were further strengthened by heat treatment in a relaxed state at temperatures near but below the flow temperature. One of the more fully characterized polymers was that from methyl-1,4-phenylenediamine and terephthalaldehyde. This polymer was spun into fiber with tenacity/initial modulus of 7.3/916 g/denier as spun. The heat-treated fiber had a tenacity/initial modulus of 38/1012 g/denier (average values).

Introduction

The literature of polymeric azomethines (Schiff bases) is extensive.[2-6] It is one of those segments of polymer chemistry in which researchers have tried repeatedly to prepare polymers with high molecular weight but in general have failed because of low solubility or infusibility of the products. In part this was due to the selection of compositions that had a low potential for tractability or ease of preparation. In some cases low to intermediate solution viscosities have been reported or molecular weights have been estimated from elemental or end-group analyses. There have been only a few reports of the successful formation of films or sintered disks.[7,8] Within this field there have been many studies of thermal stability and electrical properties of metal chelated and nonchelated products.

The first poly(azomethines) were prepared by Adams and co-workers[9] from terephthalaldehyde and benzidine and dianisidine. The products were insoluble and infusible. In the period from 1950 to 1959 Marvel and coworkers prepared a number of polyazines and poly(azomethines) from aromatic dialdehydes with hydrazine and *o*-phenylenediamine and examined their chelate formation and thermal stability.[10] Cotter and Matzner[3] have provided a summary of the literature and a table of compositions synthesized up to early 1967, and D'Alelio[2] has written a review, primarily on his work in the 1967–1968 period.

The present work describes the successful synthesis of a variety of aromatic poly(azomethines) and copoly(azomethines) by solution and melt methods. The key objective was to prepare polymers with rodlike chain structures which might be converted to high-strength fibers. The achievement of tractability has been accomplished by lowering the melting points through modification and selection of polymer structures in several ways, for example, by unsymmetrical substitution of aromatic ring units.



The above composition, coded MePPD–TA, has been studied extensively and used to prepare fibers with exceptionally high tensile properties.

Following publication of this research in patents,[11] there has appeared a series of papers by Millaud and co-workers[12] in which MePPD–TA and related polymers have been examined in terms of viscosity–light scattering molecular weight relationships, persistence length, light absorption spectra, and the formation of lyotropic solutions in sulfuric acid.

Results and Discussion

Synthetic Routes. Aromatic poly(azomethines) are very readily prepared by several routes described in the literature, the most direct being the reaction of a diamine with a dialdehyde (eq 1). The diamine will react with

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