Synthesis of soluble polyimides and functionalized imide oligomers via solution imidization of aromatic diester–diacids and aromatic diamines*

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The solution polymerization of aromatic diester–diacid monomers with aromatic diamines was investigated as an alternative to the more conventional 'two-step' dianhydride–diamine route. This method has been successfully applied to a variety of soluble polyimide systems and has proven to be a suitable route for the synthesis of controlled- or uncontrolled- (high-) molecular-weight, soluble polyimides, which exhibit high extents of imidization, M_w/M_n values of 1.9–2.0 and glass transition temperatures that are in agreement with those measured for polyimides prepared by the conventional synthesis. Acetylene-functionalized imide oligomers have also been synthesized via ester–acids. Model studies indicate that polymerization is preceded by regeneration of dianhydride from the diester–diacids.

(Keywords: polyimides; acetylene-functionalized imide oligomers; synthesis; diester–diacids; ester–acid route; solution imidization; molecular-weight control; extent of imidization)

INTRODUCTION

Polyimides are commonly synthesized from dianhydrides and diamines in a two-stage process: a soluble, high-molecular-weight poly(amide acid) is generated at low or ambient temperatures in the first stage, and is subsequently converted via bulk, chemical or solution processes to fully cyclized polyimide during the second stage[1,2].

A major disadvantage of the dianhydride–diamine route is the extreme moisture sensitivity of the initial stage; trace amounts of water may rapidly hydrolyse the dianhydride monomer and poly(amide acid), preventing the attainment of high-molecular-weight poly(amide acid). For this reason, rigorously dried glassware and carefully dehydrated solvents are absolutely essential.

Polyimides may also be synthesized from the diester–diacid derivatives of aromatic tetracarboxylic dianhydrides and aliphatic diamines[3] or aromatic diamines in solution[4]. This method has several real and potential advantages over the more conventional 'two-step' synthesis. As the product of alcoholysis is used rather than the dianhydride itself, the presence of small amounts of moisture in glassware and polymerization solvents does not present a problem, and ester–acids are generally more soluble in the polymerization solvents than are the corresponding dianhydride or tetraacids. In addition, the polymerization can be conducted using a 'one-pot' solution imidization process[5]. Unlike the conventional synthesis, the ester–acid route does not yield high-molecular-weight polymer at low temperatures; the lower initial solution viscosity in these systems is expected to provide for better fibre wetting in composite applications. An additional anticipated benefit is that ester–acids are expected to be less toxic than the analogous anhydrides.

A major purpose of this research was to determine the conditions necessary for the consistent synthesis of high-molecular-weight, fully imidized soluble polyimides utilizing the solution imidization of aromatic diester–diacids and aromatic diamines in a 'one-pot' process. Synthesis of controlled-molecular-weight polyimides with non-reactive end-groups and acetylene-functionalized, controlled-molecular-weight polyimides for use as high-T_g thermosets is currently under investigation.

EXPERIMENTAL

Materials

Phenyl benzoate (99%) and benzoic acid (99%) were obtained from Aldrich and used as received; phthalic anhydride (>99%) was obtained from Aldrich and vacuum sublimed prior to use. Diethyl phthalate, also obtained from Aldrich, was vacuum distilled before use. Aniline, *N*-methylpyrrolidinone (NMP) and 1,2-dichlorobenzene were obtained from Fisher and were vacuum distilled prior to use. *N*,*N*-Dimethylacetamide (DMAc), also obtained from Fisher, was used as received.

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Figure 1 illustrates the anhydrides used in polyimide synthesis: PMDA and BTDA were donated by Allco; ODPA was obtained from OxyChem; 6FDA was kindly provided by Hoechst-Celanese; and BPDA was obtained from Chriskev. These were monomer-grade materials and were not further purified.

The mono- and difunctional amines utilized in the polyimide synthesis are shown in *Figure 2*. Both 3,3′- and 4,4′-diaminodiphenylsulphone (3,3′-DDS and 4,4′-DDS) were obtained from Chriskev and recrystallized twice from deoxygenated ethanol before use; 4,4′-oxydianiline (4,4′-ODA), also obtained from Chriskev, was vacuum sublimed twice prior to use. 1,4-Phenylenediamine (*p*PDA) was obtained from Aldrich and was vacuum sublimed three times before use. 4,4′-Methylene dianiline (4,4′-MDA) was obtained from Aldrich and was recrystallized from benzene. 1,4-Bis(4-aminophenoxy)benzene (TPE-Q), 4,4′-bis(4-aminophenoxy)biphenyl (BAP-B) and 9,9-bis(4-aminophenyl)fluorene (FDA) were obtained from Kennedy & Klim, and 3,3′-dimethylbenzidine (3,3′-DMB) was obtained from TCI America; all were recrystallized from toluene prior to use. Bisaniline P was donated by Shell and was recrystallized from ethanol before use. The synthesis and purification of bis(3-aminophenoxy-4′-phenyl)phenylphosphine oxide (BAPPO) has been reported[6]. The 3-aminophenylacetylene (*m*APA) was donated by Eastman Kodak and was vacuum distilled before use.

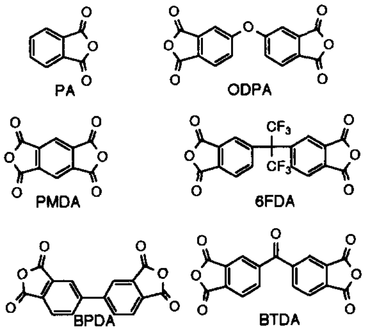

Figure 1 Anhydrides used in polyimide synthesis: PA = phthalic anhydride; PMDA = pyromellitic dianhydride; BPDA = biphenyltetracarboxylic dianhydride; 6FDA = 6F dianhydride, 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride; BTDA = benzophenonetetracarboxylic dianhydride; ODPA = oxydiphthalic anhydride

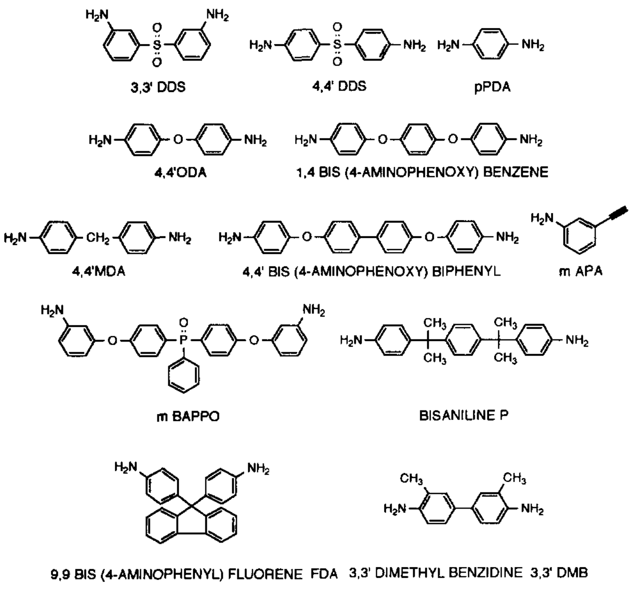

Figure 2 Diamines used in polyimide synthesis

Ester–acids were prepared by dissolving purified phthalic anhydride or monomer-grade dianhydrides in excess refluxing ethanol (7–10 ml of ethanol per gram anhydride) under nitrogen and distilling off the alcohol after a clear solution was obtained.

Model studies

The diethyl ester–diacid of BTDA (BTDE) was heated in solution to determine its behaviour under dehydrating conditions in the absence of amines. These experiments were conducted in a two-necked flask equipped with a magnetic stirrer, nitrogen inlet, thermometer, reverse Dean–Stark trap and reflux condenser; heating was provided by an oil bath. Solvents used were either 1,2-dichlorobenzene or NMP/dichlorobenzene (85/15 (vol/vol)) in sufficient amount to afford a solids concentration of 8% (wt/vol). Fourier transform i.r. spectroscopy (*FT*i.r.) was used to detect changes in the monomer structure upon heating.

In an attempt to determine whether condensation begins with attack of the amine at the carboxylic acid or ester functional group (or neither) under polymerization conditions, the synthesis of benzanilide from benzoic acid and aniline and from phenyl benzoate and aniline was attempted in NMP/dichlorobenzene (85/15 (vol/vol)) at 15% solids concentration (wt/vol). Both reactions were monitored by Fourier transform i.r. spectroscopy for the disappearance of primary amine.

The synthesis of *N*-phenyl phthalimide from monoethyl phthalate and aniline and from diethyl phthalate and aniline was also attempted, as the phthalic acid derivatives more closely resemble the diester–diacids than do the monofunctional acid and ester. Reactants were stirred in refluxing toluene for 5 h. The purpose of this study was to determine whether anhydride formation is a necessary condition for imide synthesis.

Polymer synthesis

Polymerizations were conducted as follows: monomer-grade dianhydride was introduced to a three-necked flask equipped with a magnetic stirrer, nitrogen inlet, thermometer, reverse Dean–Stark trap and reflux condenser, and heated by an oil bath. Then 7–10 ml of absolute ethanol per gram dianhydride was introduced, and the Dean–Stark trap was filled with ethanol. The mixture was then refluxed with stirring until a clear solution was obtained, at which time the trap was drained in order to collect the remaining alcohol. When the distillation of ethanol ceased, the trap was again drained and refilled with dichlorobenzene. The diamine was then introduced into the reaction vessel, followed by sufficient NMP and dichlorobenzene (85/15 (vol/vol)) to give a solids content of 15% (wt/vol). The reaction mixture was then heated to 170–180°C for 8–24 h, after which time the polymer solution was allowed to cool to ~50°C and precipitated by slowly dripping the polyimide solution into methanol or isopropanol in a high-speed blender. The polymer was isolated by filtration, air dried for 6–8 h and vacuum dried at 160–170°C for 24 h. *Figure 3* illustrates the general synthetic scheme for ODPA/3,3′-DDS polyimide.

Ethynyl-terminated polyimides were prepared using a higher solids content (e.g. 25–30% (wt/vol)) to facilitate

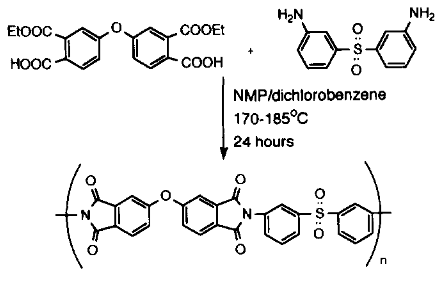

Figure 3 Polyimide synthesis

isolation; *m*-aminophenylacetylene was introduced to the reaction vessel with the diamine.

Characterization

Fourier transform i.r. spectroscopy was used to determine the presence of imide groups in the polymers; spectra were obtained with a Nicolet MX-1 *FT*i.r. spectrometer.

Titrations

Non-aqueous potentiometric titrations were employed to determine the extent of imidization of the polyimides: 1% wt/vol solutions of polymer in NMP were titrated for carboxylic acid groups with tetramethylammonium hydroxide (TMAH) in methanol using an MCI GT05 Automatic Titrator.

Intrinsic viscosity

Intrinsic viscosity measurements were utilized to monitor qualitatively the molecular weight. The evaluations were performed in NMP at 25°C using a Canon Ubbelohde viscometer.

Thermal analysis

Glass transition temperatures were determined by differential scanning calorimetry (d.s.c.) using a Perkin–Elmer DSC 7. Scans were run at a heating rate of 10°C min^{-1}; reported values were obtained from a second heat after quick cooling.

Thermogravimetric analyses were performed on a Perkin–Elmer TGA 7 Thermogravimetric Analyzer at 10°C min^{-1} in air.

Gel permeation chromatography

G.p.c. measurements were performed on a Waters 150-C ALC/GPC with viscosity detector; M_n and M_w/M_n values for several PMDA/BAPPO polyimides were determined using universal calibration.

RESULTS AND DISCUSSION

Model reactions

The diethyl ester–diacid of BTDA (BTDE) was heated in various solvents to investigate possible conversion to dianhydride in the absence of amines. Initially BTDE was dissolved in refluxing dichlorobenzene for 8 h. Several minutes after removing the reaction from heat a white solid precipitated from solution; the *FT*i.r. spectrum of this material identified it as BTDA. *FT*i.r. analysis of the dichlorobenzene revealed no carbonyl-containing compounds, either ester–acid or anhydride.

BTDE was again dissolved in dichlorobenzene, starting with a temperature of 80°C. The temperature was increased in 10°C increments and held constant for 2 h each time; aliquots were removed, placed on NaCl discs and examined by *FT*i.r. for anhydride absorbances at 1840 and 1780 cm^{-1} at 1 h intervals. The first appearance of anhydride occurred after 1–2 h at 110°C.

The experiment was repeated using NMP/dichlorobenzene to reflect more accurately the solvent system employed for polymerizations. In NMP/dichlorobenzene the conversion of ester–acid to anhydride occurs at 120–140°C; these higher temperatures may be required owing to the hygroscopic nature of the amide solvent and lower volatility of this solvent mixture relative to pure dichlorobenzene.

These results clearly indicate that anhydride can indeed be regenerated from ester–acids in solution at temperatures substantially lower than that required for quantitative imidization. However, this gave no information as to the behaviour of ester–acids in the presence of amines.

The synthesis of *N*-phenyl phthalimide from monoethyl phthalate or diethyl phthalate and aniline was investigated to determine whether amide and imide formation would occur via amine–ester condensation under normal reaction conditions. Monoethyl phthalate and aniline reacted to form *N*-phenyl phthalimide in 70% yield within 5 h in refluxing toluene; imide begins forming within 10–15 min after reflux begins. Under identical conditions diethyl phthalate and aniline failed to form amide–ester or imide. This experiment was repeated in NMP/*o*-dichlorobenzene and *o*-dichlorobenzene and as a neat reaction at 180°C for 24 h; all of these reactions also failed to yield amide–ester or imide. Similarly, phenyl benzoate and aniline failed to form benzanilide; the reactants were first heated to 150°C for 8 h. *FT*i.r. was used to monitor changes in the primary amine stretching signals, which would indicate amine consumption or amide formation, but the *FT*i.r. spectra were identical to those obtained for solutions of starting materials. The temperature was then raised to 170–180°C and maintained for 8 h. Continued observation of the *FT*i.r. spectra of the reaction mixture during this period revealed no changes (i.e. no amine consumption/amide formation). It was concluded that, under the conditions of temperature

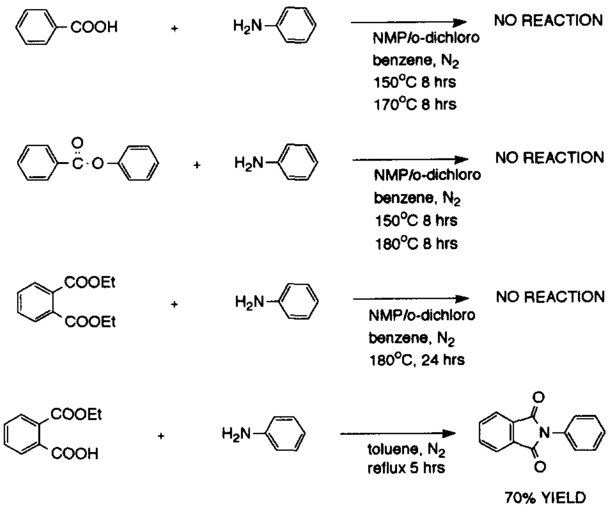

Figure 4 Model investigations of the ester–acid route

and solvent that were intended for the polymerizations, condensation of aromatic amines with aromatic esters would not occur in a reasonable period of time. These results did not rule out amine–carboxylic acid condensation, however, and this possibility was explored by monitoring the reaction of benzoic acid and aniline under the conditions of the last experiment. Again, no benzanilide was obtained. Model reactions are summarized in *Figure 4*.

These results indicate that at moderate temperatures the solution reaction of aromatic ester–acids and aromatic amines is preceded by conversion of the ester–acid to anhydride, and that blocking anhydride formation will prevent amide and imide formation. This is in agreement with reports that phthalimide can be generated from monomethyl phthalate in toluene in the presence of a tertiary amine and that tri- and tetra-esters limit the molecular weight of polyimides synthesized from ester–acid derivatives[7]. Based on these results, it was expected that a solvent system of NMP/*o*-dichlorobenzene and temperatures of 170–180°C would be suitable for polyimide synthesis.

Polymers

The ester–acid route is generally applicable to a wide variety of soluble polyimide systems. A partial list of soluble polyimides prepared by the ester–acid route and their respective intrinsic viscosities is given in *Table 1*; with few exceptions, moderate to high molecular weights may be achieved in 8–24 h.

One of the more reactive monomer combinations, 6FDA/TPE-Q, was chosen for molecular-weight control studies. Results are shown in *Table 2*. Number-average molecular weights were limited to a value of 1.5×10^4 g mol^{-1}. Molecular-weight control was effected by the following means: (1) a calculated excess of diester–diacid, (2) a calculated excess of diamine, (3) the reaction of phthalic anhydride with diamine prior to polymerization with a stoichiometric amount of diester–diacid, (4) the addition of a calculated amount of monoethyl phthalate to a 1:1 mixture of diester–diacid and diamine, and (5) the addition of monoethyl phthalate to a mixture of diester–diacid and diamine with the diamine in excess, in order to afford non-reactive end-groups.

Table 1 Reaction times and intrinsic viscosities of uncontrolled-molecular-weight polyimides

System	Time (h)	$[\eta]_{\mathrm{NMP}}^{25^\circ\mathrm{C}}$ (dl g^{-1})
BTDA/3,3′-DDS	24	0.37
BTDA/*m*BAPPO	24	0.24
BTDA/bis-P	24	1.19
BTDA/FDA	18	0.70
PMDA/*m*BAPPO	08	0.63
ODPA/3,3′-DDS	24	0.57
6FDA/3,3′-DDS	24	0.43
6FDA/*m*BAPPO	24	0.56
6FDA/FDA	18	0.55
6FDA/3,3′-DMB	18	0.86
6FDA/*p*PDA	08	0.78
6FDA/4,4′-ODA	18	1.06
6FDA/TPE-Q	08	1.05
6FDA/BAP-B	08	0.77

Table 3 PMDA/*m*BAPPO polyimides

Sample	Time (h)	Temp. (°C)	$[\eta]_{\mathrm{NMP}}^{25^\circ\mathrm{C}}$ (dl g^{-1})	M_n	M_w/M_n
1	24	180	0.56	40 000	1.91
2	16	180	0.54	35 000	1.98
3	08	180	0.63	44 000	1.92
4	05	180	0.33	–	–

These materials appeared to be completely imidized, showing strong infra-red imide absorptions at 1780, 1730, 1370 and 710 cm^{-1}, and an absence of absorptions attributable to amide acid. The intrinsic viscosities qualitatively indicate that the target molecular weight was achieved regardless of the means of molecular-weight control. Thus, the ester–acid route is a suitable method for the synthesis of controlled-molecular-weight polyimides, and monofunctional ester–acids effectively function as molecular-weight and end-group controlling structures.

As shown in *Table 3*, substantial molecular weights may be achieved within 8–24 h for the PMDA/BAPPO system; the intrinsic viscosities of ~0.5–0.6 dl g^{-1} correspond to number-average molecular weights of ~3×10^4 to 4×10^4. Perhaps more interesting, however, is the fact that the molecular-weight distribution closely approaches the theoretical value of 2 within 8 h. These materials also appeared to be completely imidized, showing strong infra-red imide absorptions at 1780, 1730, 1370 and 710 cm^{-1}, and an absence of absorptions attributable to amide acid. All except sample No. 4 form tough, transparent, flexible yellow films from DMAc.

Although *FT*i.r. is a suitable technique for detection of the imide heterocycle, a more quantitative technique employs non-aqueous potentiometric titrations to determine the amount of residual amide acid. Titration results for several 6FDA-based polyimides are listed in *Table 4*. All are highly imidized, particularly the 6F/*p*PDA polymers, display infra-red imide absorptions at ~1780, 1730, ~1370 and 710–720 cm^{-1}, and display T_g values that meet or exceed those of their counterparts synthesized via the 'two-step' process; all form transparent, flexible

Table 2 Molecular-weight control experiments

End-cap	Molar ratios of reactants, 6FDA:diamine:PA derivative	Target MW (g mol^{-1})	$[\eta]_{\mathrm{NMP}}^{25^\circ\mathrm{C}}$ (dl g^{-1})
None	1.00:1.00:0	–	1.05
6FDA	1.05:1.00:0	15 000	0.42
Diamine	1.00:1.05:0	15 000	0.45
Phthalic anhydride	1.00:1.00:0.05	15 000	0.40
Monoethyl phthalate	1.00:1.00:0.05	15 000	0.41
Monoethyl phthalate	1.00:1.05:0.95	15 000	0.42

Table 4 6FDA-based uncontrolled-molecular-weight polyimides

Sample	Time (h)	Temp. (°C)	$[\eta]^{25°C}_{NMP}$ (dl g^{-1})	Imidization (%)	T_g (°C)
6FDA/3,3′-DDS	24	180	0.43	99.0	271
6FDA/BAPPO	24	180	0.56	98.3	243
6FDA/4,4′-ODA	18	180	1.06	97.6	303
6FDA/*p*PDA	08	180	0.78	99.3	348

Table 5 Acetylene-functionalized ODPA/3,3′-DDS oligomers

Conventional synthesis			Ester–acid route		
Target *MW*	$[\eta]^{25°C}_{NMP}$ (dl g^{-1})	T_g (°C)	Target *MW*	$[\eta]^{25°C}_{NMP}$ (dl g^{-1})	T_g (°C)
5000	0.22	244	5000	0.20	244
10000	0.26	241	10000	0.22	239
15000	0.32	246	15000	0.28	242

yellow films from DMAc. Although all show extents of imidization of less than 100%, this can be explained by the presence of carboxylic acid end-groups, as none of these polymers were terminated with non-reactive end-groups. Even so, values of the order of >98% were easily achieved. To summarize, the ester–acid route is a suitable synthetic method for the synthesis of fully imidized, soluble polyimides of uncontrolled (high) or controlled molecular weights.

Acetylene-functionalized imide oligomers

Acetylene-terminated ODPA/3,3′-DDS imide oligomers were evaluated as a model system. No solid precipitated and no turbidity was observed during the polymerization, indicating that no crosslinking occurred. In addition, the isolated oligomers completely redissolve in NMP. Although the ethynyl end-groups could not be detected spectroscopically, these materials became insoluble after heating to 350°C, swelling but not dissolving in NMP. *Table 5* lists data for the ODPA/DDS oligomers; the ethynyl-terminated materials prepared by both the conventional synthesis and the ester–acid route show glass transition temperatures in the range of 240–246°C after crosslinking, slightly less than the value of 248°C measured for a high-molecular-weight linear ODPA/DDS polyimide. The intrinsic viscosities of both series of oligomers indicate that molecular weights were indeed limited, although the desired degree of molecular-weight control might not have been achieved. The difficulty in achieving the target molecular weights for this system may be a consequence of the low mutual reactivity of ODPA and 3,3′-DDS. Nevertheless, the intrinsic viscosities show the correct trend, and for a given molecular weight the intrinsic viscosities of these oligomers before crosslinking are similar regardless of the synthetic method. These results indicated that the ester–acid route should indeed be a suitable method for the preparation of controlled-molecular-weight functionalized imide oligomers.

Table 6 lists some properties for additional acetylene-terminated imide oligomers prepared by the ester–acid route. It was expected that more reactive monomer combinations would result in a greater degree of molecular-weight control and this was indeed the case, as evidenced by the intrinsic viscosities of the BTDA/3,3′-DDS, 6FDA/4,4′-ODA, 6FDA/*p*PDA, 6FDA/4,4′-MDA and BPDA/6FDA/4,4′-DDS imides. Molecular-weight control was difficult for the 6FDA/FDA system, however, and this was also attributed to low mutual reactivity of the monomers as in the ODPA/3,3′-DDS system. Again, there was no evidence of crosslinking during oligomer synthesis and heating to 400°C resulted in materials that swell but do not dissolve in NMP. The ethynyl carbon–carbon bond could not be detected by *FT*i.r. spectroscopy but all samples displayed imide absorbances at ~1780, ~1730, ~1370 and 710–720 cm^{-1} and an absence of absorbances attributable to amide acid. Measured T_g values (d.s.c.) and 5% weight losses (dynamic t.g.a.) are consistent with the respective values for the linear high-molecular-weight polyimides.

CONCLUSIONS

The synthesis of polyimides via ‘one-pot’ solution imidizations involving ester–acid and diamine monomers offers a convenient route to soluble, fully imidized, moderate- to high-molecular-weight polyimides. Only simple conditions of time and temperature are required; complex time/temperature cycles are unnecessary.

In addition, controlled-molecular-weight polyimides can be synthesized with either non-functional or functional end-groups. In particular, controlled-molecular-weight, fully imidized, soluble ethynyl-functionalized imide oligomers can be prepared without premature reaction of the ethynyl function. These oligomers crosslink to form insoluble networks, which display T_g values and weight losses comparable to their high-molecular-weight linear analogues. Model studies indicate that polymerization is preceded by regeneration of the dianhydride monomer.

CURRENT AND FUTURE STUDIES

Current and future studies include the use of additional aminophenylacetylene derivatives in the synthesis of acetylene-terminated imide oligomers, synthesis of oligomers possessing number-average molecular weights

Table 6 Acetylene-functionalized imide oligomers

System	Target *MW* ($\times 10^3$)	$[\eta]^{25^\circ C}_{NMP}$ (dl g^{-1})	T_g (°C)	5% wt loss, air (°C)
ODPA/3,3′-DDS	5	0.20	244	535
	10	0.22	239	
	15	0.28	242	
BTDA/3,3′-DDS	5	0.14	257	520
	10	0.20	255	
	15	0.28	255	
6FDA/4,4′-MDA	5	0.25	280	496
	10	0.28	292	
	15	0.34	290	
6FDA/4,4′-ODA	5	0.26	305	525
	10	0.34	303	
	15	0.45	303	
6FDA/*p*PDA	10	0.32	360	525
	15	0.40	360	
	20	0.46	364	
6FDA/FDA	5	0.17	370	530
	10	0.19	361	
	15	0.27	367	
6FDA/BPDA/4,4′-DDS	11	0.25	366	535
	16	0.35	361	
	21	0.43	364	

of less than 5.0×10^3 g mol^{-1} in order to increase T_g values and improve solvent resistance, determination of molecular-weight distributions for the soluble oligomers, and isothermal thermogravimetric analyses and mechanical testing of the crosslinked oligomers.

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