ene ethers. Various poly(ethylene ether)s containing triazine unit along the polymer backbone were prepared via nuclophilic aromatic substitution polymerization. These polymers were characterized by high glass transition temperatures of 200–260°C with high thermal stability. Thus, the triazine-based polyarylene ethers may be a candidate for high-performance plastic materials.

REFERENCES AND NOTES


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Macromolecular Engineering of Polylactones and Poly(lactides). XV. Polylactides (PLA) and Poly(lactides) (PLDLAs) as Precursors of Biocompatible Graft Copolymers and Bioerodible Gels

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SYNOPSIS

The functional aluminum alkoxide, B3Al — O — (CH3) inaug O — C(CH3) inaug C2H5, is a very effective initiator for the (S,L)-lactide (LA) polymerization in toluene at 70°C. The coordination-insertion type of polymerization is living and exclusively yields linear P(D,L)-lactide macromonomers of a predictable molecular weight and a narrow molecular weight distribution. 1H and 1H-NMR studies show that the methacryloyl group of the initiator is selectively and quantitatively attached to one chain end, whereas the second extremity is systematically a hydroxyl function resulting from the hydrolysis of the living growing site. α,ω-Dimethacryloyl P(D,L)-lactides, i.e., α,ω-macromonomers, have also been successfully synthesized by the additional control of the termination step, i.e., by reaction of Alalkoxide end groups with methacryloyl chloride. α-Macromonomer and α,ω-macromonomer P(D,L)-lactides are easily free-radical copolymerized with 2-hydroxyethyl methacrylate (HEMA), resulting in a hydrophilic poly (HEMA) backbone grafted with hydrophobic P(D,L)-lactide subchains and a biodegradable amphiphilic network, respectively. © 1994 John Wiley & Sons, Inc.

Keywords
poly(lactide) · macromonomer · ring-opening polymerization · graft copolymers · amphiphilic gel · biocompatible

INTRODUCTION

During the last decade, special attention has been paid to the well-controlled synthesis and through characterization of macromonomers and to their ability to undergo copolymerization with acrylic and vinyl comonomers. Actually, a large variety of macromonomers has been prepared as precursors of graft copolymers of great potential as coatings, adhesives, compatibilizers, emulsifiers, biomaterials, etc. 1, 3 Poly(lactide) macromonomers are expected to play an increasingly important role in the biomedical field. Indeed, poly(lactides) (PLA), polylactide (PGA), and their copolymers form a family of biodegradable and bio-compatible polymers that are widely used in biomedical applications, such as absorbable sutures, 3, 4 biomaterials, 3, 4 sustained drug delivery systems, and absorbable fibers. 1, 3 These linear aliphatic polyesters are mainly synthesized by ring-opening polymerization of the corresponding cyclic diesters, i.e., lactides (LA) and glycolide (GA).

It has been reported elsewhere that aluminum alkoxides are effective initiators for the controlled polymerization of lactones, 2, 3 lactides, 2, 3 and cyclic anhydrides 3 with formation of polysters and poly(lactides) of a very narrow molecular weight distribution. For example, lactides can be polymerized by Al(O(R)3) in toluene, at 70°C, according to a "coordination-insertion" mechanism which involves the insertion of the lactide into the "Al — O" bond.

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1 "Chimie de Recherches" by the Belgian National Foundation for the Scientific Research (FNSR).
2 To whom all correspondence should be addressed.
3 © 1994 John Wiley & Sons, Inc.
of the initiator and the selective acyl-oxygen cleavage of the monomer (eq. (1), R = -Pr):

Furthermore, functional aluminum alkoxides, such as (C₆H₅)₃Al(OR), where X is a functional group, have been proven to be very successful in the synthesis of end-reactive polycaprolactone (PCL) and PLLA. One end-group of the polyester is systematically an alkoxide and thus an alcohol after hydrolysis of the growing species [see eq. (1)] and the second extremity is quantitatively capped with an ester, the alkoxide radical of which is nothing but the "ORX" alkoxide group of the initiator (X: halogen, tertiary amine, unsaturation, etc.).

This article deals with the synthesis of well-defined α-methacryloyl PLA and α,ω-dimethacryloyl PLA (di)macromonomers from functional diethylaluminum alkoxides. Unsaturated alkoxides have been synthesized on purpose from the equimolar reaction of triethylaluminum with 2-hydroxyethyl methacrylate (HEMA). The discussion will mainly focus on synthetic problem, polymerization kinetics, and control of the end groups. Potentials of these (di)macromonomers in copolymerization with unsaturated comonomers, such as 2-hydroxyethyl methacrylate (HEMA) will be considered as an access to bioadhesive amphiphilic graft copolymers and gels. The use of a (di)macromonomer for the synthesis of polymer networks with tailored properties has recently been described by one of us.15

**EXPERIMENTAL**

**Materials**

(ω,ω)-lactide (LA) was purchased from Boehringer and recrystallized three times from dried ethyl acetate at 60°C. The monomer was dried for 24 h at 35°C, under reduced pressure (10⁻³ mm Hg) before polymerization. The resulting purity of (ω,ω)-LA (mp 127°C) was higher than 99.9% as shown by gas chromatography and nucleosil tetratritium revealed a residual acid content lower than 10⁻⁴ mol%. Triethylaluminum (TETRA) was purified by distillation under reduced pressure and dissolved in dry toluene. Solution concentration was determined by a 2N complexometric titration of Al by EDTA. 2-Methyl-2-oxo-1,3-oxazine methacrylate (HEMA) (Jansen Chimica) and pyridine (Aldrich) were dried over CaH₂ and KOH, respectively, for 48 h and freshly distilled under reduced pressure. Toluene, ethyl acetate, and tetrahydrofuran (THF) were dried by refluxing over CaH₂ and CaCl₂ and a benzophenone-sodium complex, respectively.

**Polymerization Procedure**

**Homopolymerization of (ω,ω)-LA**

Synthesis and characterization of initiator 1 was reported elsewhere.16 Polymerization took place under stirring, in toluene at 70°C. (ω,ω)-lactide was insoluble in toluene. The monomer was added into the reactor in a glove box under a nitrogen atmosphere. Solvent and initiator were then successively added with a syringe pump or a stainless-steel cylinder through a rubber septum. The reaction was stopped by adding an excess (relative to the initiator) of HCl solution. P(ω,ω)-LA known to be hydrolytically sensitive, was then precipitated into an excess of cold methanol, filtered, and dried under vacuum to a constant weight.

For the polymerization reaction, the PLA macromonomer 4 was synthesized according to the homopolymerization recipe. Initiator 1 was used and the aluminum alkoxide end groups were reacted with methacryloyl chloride instead of being hydrolyzed. When the monomer conversion was complete, toluene was distilled off and substituted by the same volume of dried THF. An excess of 10 equiv of methacryloyl chloride and pyridine in THF was slowly added to the PLA solution at 50°C. After 30 h, the polymerization medium was hydrolyzed, filtered, and the PLA α,ω-macromonomer 4 was recovered by precipitated polymerization in cold methanol. The α,ω-macromonomer 4 was purified as previously described.

**Copolymerization of HEMA with P(ω,ω)-LA**

Macromonomer 3

α-Methacryloyl-ω-hydroxy-PLA macromonomer 3 (M = 4300, 0.5, 0.12 mmol), freshly distilled HEMA (0.5 g, 9.9 mmol), and AIBN (50 mg) were dissolved in DMF and stirred for 24 h at 60°C. DMF was distilled off and the crude copolymerization product was redissolved in THF, and precipitated in heptane. It was filtered, dried overnight under reduced pressure, and analyzed by IR, 'H-NMR, and SEC. It will be designated as "graft" copolymer 5.

**Copolymerization of HEMA with α-Methacryloyl-P(ω,ω)-LA dimacromonomer 4**

α-Dimethacryloyl-PLA dimacromonomer 4 (M = 2150, 0.5, 0.42 mmol) and AIBN (75 mg) were dissolved in freshly distilled HEMA (3.0 g, 23.1 mmol) under stirring. This solution was poured into a teflon mold, and kept at 60°C for 30 h. The disk-shaped gels were removed, dried under vacuum at 70°C for 1 day, and weighed (w₀) They were then step-wise extracted with THF (50 mL) and methanol (50 mL) respectively. They were finally dried and weighed (w₁). The gel fraction was calculated as w₁/w₀ × 0.78. Swelling was measured at room temperature by plunging cubic-shaped samples (w₂ = 0.3 g) into 50 mL of buffered water (pH 7.15), and chloroform, respectively. After various periods of time, gels were weighed (w₃) and the solvent content was calculated as w = (w₀ - w₁ - w₃)/w₀ × 100%.

**Measurements**

IR spectra were recorded with a Perkin-Elmer IR 1200. 'H-NMR spectra of PLA were recorded in CDCl₃ with a Bruker AM 400 apparatus at 25°C. Molecular weight and molecular weight distribution were determined by size exclusion chromatography. GPC Hewlett-Packard 1000 chromatograph was used in THF and calibrated with polystyrene standards. Calibration for P(ω,ω)-LA was set up from the appropriate viscometric relationships in THF at 30°C. Molecular weights of oligomers were also calculated by 'H-NMR from the relative intensity of the signals of the methacryloyl end group and the methine ester groups of the polyester chain. A good agreement was usually observed between Mₑ obtained by SEC and NMR.

**RESULTS AND DISCUSSIONS**

**Synthesis of PLA Macromonomers**

Dietyaluminum 2-hydroxyethyl methacrylate 1 is prepared by substitution of one ethyl group of AIBN by freshly distilled 2-hydroxyethyl methacrylate (HEMA) [eq. (2)]

The structure of resulting compound 1 is confirmed by 'H NMR spectroscopy as previously reported.17 The P(ω,ω)-lactide polymerization is initiated by the AIBN 1, used in various molar ratios with respect to the monomer. Polymerization is carried out in toluene solution at 70°C. After hydrolysis of the reaction medium, the final polymer is recovered by precipitation in cold methanol and analyzed by SEC, 'H-NMR, and IR spectroscopy.

A typical size exclusion chromatogram of a P(ω,ω)-LA macromonomer is shown in Figure 1. This particular sample corresponds to a monomer to molar ratio of 14 to 1 monomer conversion of 96% (96 h at 70°C). The molecular weight distribution is relatively narrow (M₅/M₁ = 1.2, M₅ = 950). No peak due to cyclic oligomers can be detected in the low molecular weight region.

As shown in Figure 2, the number-average molecular weight (M₅) of the polymer increases linearly with monomer conversion, although the polymolecularity is nearly constant at 1.1 to 1.2. This observation is in favor of a living polymerization, which is convincingly assessed by the linear dependence of DP [monomer/ initiator] molar ratio (Fig. 3). Since the slope of this plot is close to 1, it is obvious that each of the alkoxide group initiates the lactide polymerization at 70°C. Molecular weight
To confirm unambiguously that P(1,LA) is selectively and quantitatively coupled by the vinylidene acryloyl radical of the initiator 1 the recovered polymer has been characterized by 1H-NMR (Fig. 4) and IR (Fig. 5) spectroscopies. The absorbance at 1638 cm⁻¹ is consistent with the presence of a carbon–carbon double bond (Fig. 5). The same qualitative conclusion is supported by the 1H-NMR signals and their relative intensity at 5.60 (J = 0.55) and 6.12 ppm (J = 0.57) consistent with the 3-hydroxypropane protons at δ = 3.45 ppm (J = 0.56) (Fig. 4).

From the nature of the end groups, i.e., a methyl acryloyl group and a hydroxyl function, respectively, it must be concluded that the lactide is inserted as the AL — O bond of the initiator through the selective cleavage of the acyl–oxygen bond of the monomer:  

\[
\begin{align*}
&\text{CH}_2=\text{CH}-\text{CO}-\text{CH}_2-\text{O}-\text{C(OH)}-\text{O}\ldots
\end{align*}
\]

At our best knowledge, it is the first time that polylactide macromonomers have been proposed with a predictable molecular weight and a narrow molecular weight distribution. Moreover, these results are in a perfect agreement with the c-CL polymerization initiated with the same functional diethylaluminum alkoxide 1. As a result, the sequential addition of c-CL and (1,LA) to initiator 1 in toluene at 25 and 70°C, respectively, successfully leads to the expected diblock P(1,LA) macromonomers where, once again, the molecular parameters are perfectly controlled.

It is known that, when the polymerization medium is kept at 70°C beyond the time required for the complete lactide conversion, the molecular weight distribution starts to broaden. This effect is more likely due to side transesterification reactions. An increase in the polymerization time enhances the deleterious effect of transesterification and the loss of control on the molecular characteristics of PLA chains. Accordingly, kinetics of (1,LA) polymerization has been investigated by a statistical method as described elsewhere.

After a typical induction period (ca. 1 h), the polymerization is first order in monomer as shown by a linear relationship between monomer conversion (ln[LA]/[LA]₀) and polymerization time (Fig. 6). The induction period is systematically observed when the polymerization of c-CL and (1,LA) is promoted by Al alkoxides. A recent study of the "coordination-insertion" mechanism using 13C- and 31P-NMR spectroscopy, cryoscopy, and viscometry has shown that this initial period has to be attributed to a complete dissociation of the coordinative aggregates of the initiator in toluene upon addition of the monomer. Polymerization of (1,LA) is also first order in initiator 1 as shown in Figure 7. Except for the induction period, kinetics of (1,LA) polymerization obeys as simple kinetic law:

\[
\frac{d[LA]}{dt} = k[LA]/[AI]
\]

where \( k \), the kinetic constant is 1.58 × 10⁻² L mol⁻¹ min⁻¹ in toluene at 70°C. The same kinetic behavior has been observed for the lactide polymerization initiated by Br₃(CH₂)₃—OAlEt₂ and H₂C—CH(CH₂)₄—OAlEt₂ under the same experimental conditions. Using these two initiators, the kinetic constants \( k \) are 1.1 × 10⁻² and 1.0 × 10⁻² L mol⁻¹ min⁻¹, respectively, supporting that the functional groups under consideration are of a very limited effect on the "Et₃Al—O-" active species.
Figure 4. $^1$H NMR spectrum of P(D,L)-LA ($\bar{M}_n = 3700$) as recovered after hydrolysis of P(D,L)-LA initiated by diethylaluminum alkoxide 1 (solvent: CDCl$_3$):

<table>
<thead>
<tr>
<th>Protons</th>
<th>$\delta$ (ppm)</th>
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<tr>
<td>a</td>
<td>6.12</td>
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<tr>
<td>b</td>
<td>5.60</td>
<td>0.55</td>
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<td>c</td>
<td>5.94</td>
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<tr>
<td>d</td>
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<td>f</td>
<td>5.20</td>
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This observation is only valid when diethylaluminum alkoxides are considered. Indeed, rate constants of the e-CL and LA polymerization as initiated by Al trialkoxides, are directly affected by the nature of the alkoxide group (functional or not). This kinetic behavior, which is at least partly con

Figure 5. IR spectrum of P(D,L)-LA ($\bar{M}_n = 1950$) as recovered after hydrolysis of P(D,L)-LA initiated by diethylaluminum alkoxide 1.

Figure 6. Order in monomer for the polymerization of (D,L)-LA initiated by diethylaluminum alkoxide 1 in toluene at 78°C. $[\text{LA}]_0 = 0.05$ mol L$^{-1}$; $[\text{Al}] = 1.15 \times 10^{-2}$ mol L$^{-1}$ (I), $1.58 \times 10^{-3}$ mol L$^{-1}$ (II), and $3.0 \times 10^{-3}$ mol L$^{-1}$ (III).
As an example, (d,l) LA has been polymerized in toluene at 70°C by using the Al monokiloide I as an initiator ([LA]₀/[AI] = 25), followed by reaction with methacryloyl chloride. After hydrolysis, the quantitatively recovered PLAs with functional macromonomers (ω-ω-dimethacryloyl PLAs or ω-µ-methacryloyl PLAs) 4 has been characterized by 1H-NMR (Fig. 8). Signal at 4.55 ppm of the ω-hydroxy-thiol protons (see Fig. 4) has been shifted to lower field (δ H = 5.20 ppm). Furthermore, extra signals observed at δH = 6.07 and δH = 5.56 ppm can be assigned to the second methacrylic unsaturations, which is in a slightly different chemical environment compared to the first one. The experimental molecular weight of PLA chains—3580 and 3800—is determined by 1H-NMR and SEC, respectively, and is in a good agreement with theoretical M, = 3600. Molecular weight distribution remains relatively narrow (M, // M, = 1.2), confirming the absence of degradation reactions.

Synthesis of "Graft" Copolymers from P(d,l) LA Macromonomers

P(d,l) LA macromonomers 3 have been copolymerized in a free radical process by HEMA, which

\[
-k = 1.58 \times 10^{-2} \text{mol}^{-1}\text{L}^{-1}\text{min}^{-1}
\]

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is the precursor of a biocompatible and hydrophilic polymer. A \( \omega \)-methacryloyl-\( P(\omega,\omega) \text{LA} \) macromonomer 3 (\( M_0 = 4500, M_\infty / M_0 = 1.1 \)) has been copolymerized with HEMA in dimethylformamide (DMF) at 60°C for 24 h, by using azo-2,2'-bis (isobutyronitrile) (AIBN) as a free-radical initiator:

\[
\begin{align*}
\text{HEMA} & \quad \text{DMF, 60°C, 24 h} \\
\text{AIBN} & \quad \text{5 \( (M_\infty = 4500) \)}
\end{align*}
\]

When DMF is replaced by THF, a nonsolvent of poly(HEMA), a clear solution is obtained which indicates that no poly(HEMA) is formed, at least at a structural unit ratio [nHEMA/(\( \omega,\omega \) LA units)] of 1.95. That the whole \( P(\omega,\omega) \text{LA} \) macromonomer is copolymerized is confirmed by the absence of the unsaturation signals in the IR and \( ^1H \)-NMR spectra (Figs. 9 and 10).

Composition of the resulting "graft" copolymer 5 has been determined from the polymerization degree of the poly lactide macromonomer (DP = 30), and the relative intensity of the methine protons (\( \delta H_1 = 5.25 \) ppm) in the PLA subchains and the \( \omega \)-hydroxy methylene protons (\( \delta H_3 = 3.96 \) ppm) in the polyhydroxylate chains (Fig. 10). The experimental final ratio (n/HEMA) of 2.05 is in a very good agreement with the initial value (1.85). It may be noted that tacticity of the copolymer backbone is predominantly syndiotactic groups (\( \geq 85\% \)) (\( \delta H_1 = 1.40 \) ppm and \( \delta H_3 = 2.15 \) ppm) compared to the heterotactic methyl groups (\( \leq 15\% \)) (\( \delta H_3 = 1.46 \) ppm and \( \delta H_1 = 2.25 \) ppm). A very similar tacticity has previously been reported by De Visser et al. for homopolymerization of HEMA initiated by AIBN in ethanol at 60°C. As expected, these amphiphilic graft copolymers display interesting surfactant properties. As an example, as small as 1.25 wt % of copolymer 5 (\( M_\text{PLA} = 4500, \text{HEMA} / \text{LA} = 2.05 \)) is able to stabilize a toluene/water (1/3) emulsion over a period of at least 10 days. Use of these graft copolymers as surface active agents in emulsions and polymer-stabilized colloids will be the topic of a forthcoming paper.

Synthesis of Biodegradable and Biocompatible Amphiphilic Networks

Crosslinked hydrophilic polymers or hydrogels are extensively used in the controlled-release of drugs. Most of these hydrogels, however, are non-biodegradable and the drug release is mainly controlled by diffusion. Interestingly enough, biodegradable and biocompatible hydrogels could be obtained by free-radical copolymerization of P(\( \omega,\omega \) LA) \( \omega \)-\( \omega \)-macromonomers (4) with HEMA, as shown by eq. (5).

\[
\begin{align*}
\text{HEMA} & \quad \text{DMF, 60°C, 24 h} \\
\text{AIBN} & \quad \text{Hydrolysis}
\end{align*}
\]

Drug release mechanism, degradation rate and physical properties of these hydrogels can be tailored by the appropriate choice of macromonomer molecular weight and composition of the copolymers.

Based on an initial (HEMA/LA) unit ratio of 3.7, the free-radical copolymerization of HEMA and PLA \( \omega \)-\( \omega \) macromonomers (4) (\( M_0 = 2136, M_\infty / M_0 = 1.13 \)) leads to the formation of a bicomponent network. After 30 h polymerization at 60°C, the crosslinked material has a gel fraction (\( u_h / u_f \)) of 0.78 (see Experimental section). Indeed, selective extractions by methanol and THF, respectively, have allowed 8.5 wt % of P(HEMA) and 13.5 wt % of poly lactide chains end-capped with a few HEMA units to be isolated.

Due to the amphiphilic character of the network, swelling behavior has been studied in water and in an organic medium: chloroform. For a network pre-

Figure 9. IR spectrum of the P(HEMA-g-(\( \omega,\omega \) LA)) "graft" copolymer 5 [see eq. (7)].

Figure 10. \( ^1H \)-NMR spectrum of the P(HEMA-g-(\( \omega,\omega \) LA)) "graft" copolymer 5 [see eq. (7)]. Solvent = pyridine/CDCl\text{3} (9/1).
pared from an initial (HEMA/LA) unit ratio of 3/7 and M, P(DDLLA) of 2150, the solvent content (see Experimental section) is 34.0 ± 2.0%, and 50.0 ± 0.5% in water and in chloroform, respectively. It is clear that these novel amphiphilic networks are suitable for a number of biomedical applications, such as macromolecular drug delivery systems. Indeed, drugs can be easily incorporated either during the free radical copolymerization or by swelling with an organic solvent. Furthermore, these biocompatible gels are biodegradable. When swelling occurs in distilled water, water pH decreased from neutral to ca. 3.7. This acidity increase might result from the release of lactic acid as a result of the hydrolysis of polylactide chains [see eq. (8)]. Similar observations have been recently reported for bioerodible hydrogels based on poly(ethylene glycol)-co-poly acryloyl hydroxy acid. Extensive studies of the ability of (HEMA-co-L or DDLLA) gels to control drug release is under current investigation. Effect of composition of the comonomer feed, molecular weight of polylactide chains and nature of the hydrophilic comonomer, e.g., HEMA, acrylamide, and N-vinyl pyrrolidone, will be related to the degradability and the swelling behavior of the resulting poly/ hydrogels.

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Synthesis of Thermotropic Liquid Crystal Polymide and Its Properties

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SYNOPSIS

Thermotropic liquid crystal polymeide which has neither an ester linkage nor a carbonate linkage was prepared by the polymerization of 1,2,4,5-benzenetetracarboxylic dianhydride (PMDA) and 1,3-bis[4-(4-aminophenoxy)benzyl]benzene (BACB). This polymeide shows the liquid crystal phase at 549-593 K. Mixing this liquid crystal polymeide or copolymerizing BACB decreases the melt viscosity of the thermoplastic polymeide (Aurm). © 1994 John Wiley & Sons, Inc.

Keywords: thermotropic liquid crystal polymeide

INTRODUCTION

Polymeides are one of the most useful super engineering plastics and is characterized by high thermal stability, good chemical resistance, and high mechanical properties. But polymeide encounters serious difficulties in melt processing because of its high glass transition temperature and high melting temperature. There are three methods for producing the melt processable polymeides. The first is by the introduction of a flexible connecting linkage to the backbone, the second is by introducing unsymmetrical structures to the backbone, and the third is copolymerization. Our result in producing the melt processable polymeide is Aurum which is produced by the reaction of 1,2,4,5-benzenetetracarboxylic dianhydride (PMDA) with 4,4′-biphenyl(4-aminophenoxy) biphenyl (BAPP). This thermoplastic polymeide Aurum has a flexible connecting linkage and unsymmetrical structures. This polymeide can be used for injection or extruding molding, films, fibers, and composites with fibers. But this melt processable polymeide has a high melting temperature; thus, the melt processability is insufficient for certain uses. For improving melt processability, soft segments were introduced to backbone structures and the number of inside linkages per repeating unit was reduced. In this article we report the physical properties of the polymeides prepared using diamines having five benzene rings.

EXPERIMENTAL

1,3-Diaminobenzene (mp 336 K, Mitsui Toatsu Chemicals, Inc.), 1,4-diaminobenzene (mp 420-421 K, Mitsui Toatsu Chemicals, Inc.), and 1,3-bis[4′-(4-aminophenoxy)benzyl]benzene (mp 404-406 K), 1,3-bis[4′-(4-aminophenoxy)benzyl]benzene (mp 387-388 K), 1,3-bis[4′-(4-aminophenoxy)phenoxyl]benzene (mp 379-380 K), 1,3-bis[4′-(4-aminophenoxy)benzyl]benzene (mp 370-380 K), 1,3-bis[4′-(2-trifluoromethyl-4′-aminophenoxy)benzyl]benzene (mp 391-392 K), 1,3-bis[4′-(2-cyano-4′-aminophenoxy)benzyl]benzene (mp 464-465 K), 1,3-bis[4′-(2-methyl-4′-aminophenoxy)benzyl]benzene (mp 391-392 K), and 1,3-bis[4′-(3-methyl-4′-aminophenoxy)benzyl]benzene (mp not observed), and bis[4′-(2-methyl-4′-aminophenoxy)benzyl]benzene (mp not observed) were prepared by reduction of dinitro compounds which were produced from corresponding

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