Fluidity Improvement of Semiaromatic Polyamides: Modification with Oligomers

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ABSTRACT: Poly(decamethylene terephthalamide) PA10T with different relative viscosities (RV) were successfully produced by the reaction of 1,10-decanediamine and terephthalic acid through molecular weight regulator benzoic acid (BA). RV was shown to be decreased linearly with increasing BA concentrations and detailed structures of PA10Ts were characterized by ^{13}C-NMR. Fluidity of PA10T with varying molecular weight was tested and low RV PA10Ts were used as modifiers to improve fluidity behaviors of high RV PA10Ts, meanwhile mechanical properties were maintained. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40058.

INTRODUCTION

Combining both high melting points of wholly aromatic polyamides and good melt processability of aliphatic polyamides, semiaromatic polyamides have attracted much attention in recent years. Such semi-aromatic polyamides perform excellent in heat resistance and dimensional stability, as compared with aliphatic polyamides such as nylon 6 and nylon 66. Accordingly, by taking advantage of such properties, semiaromatic polyamides are widely used particularly in the fields of electric/electronic components and molded articles for automobile components.[1–7]

The homopolymer of poly(hexamethylene terephthalamide) (PA6T) has an excessively high melting point, as high as 370°C, and hence the thermal decomposition of PA6T at the time of melt processing thereof cannot be suppressed. Accordingly, PA6T is used under the conditions that the melting point thereof is sufficiently decreased by introducing a large amount of a copolymerization component.[8–12] However, in such copolymerized PA6T, the crystallinity is impaired and a high-crystallinity molded article has not been able to be obtained at a rapid crystallization rate. Meanwhile, another solution is increasing the carbon-chain length of the aliphatic diamine, which not only reduces melting points of semiaromatic polyamides but also lowers water absorption of them.[13–18] For example, Poly(decamethylene terephthalamide) (PA10T) melts at 316°C, and its water absorption is only about one third of that of PA6T/66.[10,19] Low water absorption is proved to be a critical property for a heat-resistant material applied in surface mount technology (SMT) components.[20–24] High water absorption materials intend to blister during the heating process of SMT, and in many cases they absorb so much moisture when exposed to high-humidity conditions that they blister at temperatures that are too low to be practical.[25]

Indeed, including excellent heat resistant properties, these thermoplastic compositions must be sufficiently fluid when they are in the molten state in order to be able to be conveyed and handled easily and rapidly in some forming devices such as, for example, injection molding.[6,26–31] However, fluidity insufficiency of PA10T compared with PA6T-related polyamides becomes a threshold because a great deal of moulding articles are thin-walled and only polyamides with high fluidity can meet this requirement. Theoretically speaking, molecular weight reduction can lead to fluidity improvement; however, mechanical properties deterioration is often inevitable simultaneously.

Herein, PA10T oligomers were successfully produced by regulating concentration of end-capping agent and the products were characterized by ^{13}C-NMR. The effect of the concentration of end-capping agent on oligomers molecular weights was studied. Finally, a PA10T oligomer with moderate molecular weight was chosen as a flow modifier to increase the fluidity of high molecular weight PA10T and meanwhile mechanical properties of the products were maintained.

Table I. Polymerization Results at Different BA Concentrations

		Prepolymer		Polymer		
Run	BA/TA	[NH$_2$]/mol/t	[COOH]/mol/t	[NH$_2$]/mol/t	[COOH]/mol/t	RV
1	0.04	1633	1599	45	129	2.135
2	0.05	1519	1556	40	135	1.914
3	0.07	1551	1582	41	140	1.744
4	0.10	1709	1678	47	130	1.515
5	0.12	1658	1699	48	137	1.326

EXPERIMENTAL

Materials

Terephthalic acid, 1,10-diaminodecane and benzoic acid (BA) were purchased from Guangzhou Chemical Reagent Factory. Hexafluoroisopropanol (HFIP), concentrated sulfuric acid (96%) and chloroform-*d* (CDCl$_3$) were purchased from J&K Chemicals.

Synthesis

Synthetic procedure of run 1 in Table I is as follows, and other products of Table I can be produced in a similar way by varying benzoic acid concentration.

Prepolymerization

A 20 L autoclave was charged with terephthalic acid (2960 g), 1,10-diaminodecane (3200 g), benzoic acid (82.8 g), sodium hypophosphite (6.2 g) and deionized water (2550 g). The autoclave agitator was set to 0 rpm and the contents were purged with nitrogen at 10 psi for 10 min. Then the autoclave was heated to 225°C and during the heating process the agitator was set to 50 rpm and rotated at about 180°C. The temperature reached 250°C after about 3 h and was held there for about 40 min, after which water discharge was carried out to release 1650 g of water condensated by a reflux condenser through 1 h. Then the reaction product formed in the reaction vessel was flushed into the open air through a nozzle to take it out in a solid form which was then dried to obtain a solid low-degree condensation product. The low-degree condensation product could be easily taken out without being adhered to the wall surfaces or to the discharge port.

Postcondensation

Five kilograms of the low-degree condensation product of the aromatic polyamide was thrown into a vacuum tumbler dryer having an effective volume of 20 L. The low-degree condensation product of the aromatic polyamide was heated up to 240°C in 5 h while rotating the tumbler at 10 rpm and vacuum degree at 20 Pa. During the tackifying process, the sample was taken in an interval time of 40 min, which was then used for terminal group concentration test until amino concentration decreased to 40–50 mol/t and then vacuum was replaced by nitrogen, and meanwhile cooling program began.

Preparation of Modified Resin Compositions

The components were blended in dry with a ratio shown in titles of Table II. Additives including antioxidant and lubricant are added with the same ratio for all of them (0.5 wt %+0.5 wt %), and the rest component is supplemented by resins. The resulting blend was subjected to a twin-screw extruder and extruded in melt under the condition of the cylinder temperature of 330°C. The melt strands were cooled and cut in pieces to give pellets of a polyamide composition. The pellets were dried in vacuum at 120°C. for 12 h and the dried pellets were subjected to injection molding under the condition of the cylinder temperature of 320°C and mold temperature of 100°C to give a test piece having a determined shape.

Table II. Compositions and Mechanical Properties of Compounds Based on Semi-Aromatic Polyamides Blended with Oligomers/Prepolymers, TiO$_2$, and talc

		1#	2#	3#	4#
Polyamide Composition	PA10T/wt %	60	0	45	57
	PA6T/66/wt %	0	60	0	0
	Ti-Pure R-105/wt %	30	30	30	30
	Talc-1250 mesh/wt %	10	10	10	10
	O$_{1.5}$/wt %	0	0	15	0
	Pre/wt %	0	0	0	3
Mechanical Properties	Tensile strength/MPa	57 ± 2	68 ± 3	52 ± 2	46 ± 2
	Elongation at break/%	3 ± 0.2	3.5 ± 0.2	3 ± 0.2	2.4 ± 0.2
	Flexural strength/MPa	107 ± 6	121 ± 7	105 ± 6	91 ± 5
	Flexural modulus/MPa	4700 ± 200	5600 ± 250	4900 ± 200	4600 ± 200
	Impact strength, IZOD notched/kJ/m^2	4.8 ± 0.3	6.8 ± 0.4	4.3 ± 0.3	3.5 ± 0.2
	Impact strength, IZOD unnotched/kJ/m^2	20 ± 1	28 ± 1.5	21 ± 1	12 ± 0.7

Characterization

Content of Amino End Group. An automatic potentiometric titrator is used to measure the concentration of amino end group. 0.5 g polymer, 45 mL phenol, and 3 mL absolute methanol are added into a 100-mL conical flask putting on an electric heat plate to heat this mixture to reflux until the sample dissolves completely. After cooling to room temperature, the solution is titrated by calibrated hydrochloric acid standard solution to get amino group concentration.

Content of Carboxyl End Group. An automatic potentiometric titrator is used to measure the concentration of carboxyl end group. 0.500 g polymer and 50 mL o-cresol are added into a 100 mL conical flask putting on an electric heat plate to heat this mixture to reflux until the sample dissolves completely. After cooling to room temperature, the solution is titrated by calibrated KOH-ethanol solution to get carboxyl group concentration.

Relative Viscosity. The proper amount of 98% sulfuric acid is placed with a pipette into a volumetric flask, after which 0.25 g sample is added. Then the flask is put in a shaking table with water bath of 50°C for about 1 h until the sample is dissolved completely. The flask is put in a constant temperature bath, and allowed to reach 25°C. Then the sulfuric acid solution is diluted to 25 mL and dumped into an Ostwald viscometer. The time required for the upper meniscus to successively pass the two calibration marks of this instrument is recorded as t_1, and the efflux time of pure sulfuric acid is recorded as t_0. Then relative viscosity can be calculated as: $RV = t_1/t_0$.

^{13}C-NMR Characterization. NMR samples containing 10 wt % polymers in a 3 : 1 volume ratio of hexafluoroisopropanol (HFIP) to $CDCl_3$ were prepared by dissolving polyamide in HFIP, followed by addition of $CDCl_3$. Solution ^{13}C-NMR spectra were collected on a BRUKER AVANCE400 spectrometer operating at a frequency of 100.6 MHz. All spectra were recorded at 25°C with decoupling implemented only during data acquisition. The number of transients required to achieve sufficient signal-to-noise for end-group identification ranged from 5000 to 18,000, depending on molecular weight. Baselines were corrected using a 10th order polynomial.

Melt Viscosity of Polyamide. The melt viscosity was measured with LCR-7000, produced by Dynisco, using die type CZ394-20 at 330°C, and a melt retention time of 5 min. The shear rate is from 500 to 5000 s^{-1}.

Mechanical Test

Tensile strength and elongation at break: Measured in compliance with ISO 527-2 at 23°C under a speed of 10 mm/min using 1A type specimen; Flexural strength, and flexural modulus: Measured in compliance with ISO 178 at 23°C under a speed of 2 mm/min using specimen 80 × 10 × 4 mm^3; Impact strength (IZOD notched) : Measured in compliance with ISO 180 at 23°C using A type specimen; Impact strength (IZOD unnotched) : Measured in compliance with ISO 180 at 23°C using U type specimen.

RESULTS AND DISCUSSION

Synthesis and Characterization of PA10T Oligomers

PA10T polymers were prepared from the reaction of 1,10-decanediamine (DA) and terephthalic acid (TA) through a two-step
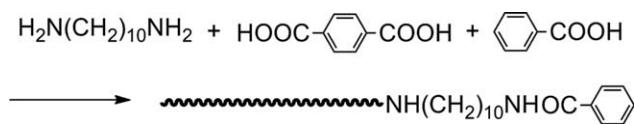
Scheme 1. BA as a molecular weight stabilizer in PA10T synthesis.

procedure: prepolymerization and solid state polymerization (SSP). Some academic researchers usually produced a 10T salt to assure an accurate equivalent ratio of amine to acid using ethanol as a solvent[32] before prepolymerization was conducted, which was actually unnecessary due to the volatilization of DA, viz., whether or not 10T salt is produced, a slight excess of DA must be added to compensate its loss during water discharge process in prepolymerization. In addition, safety risk and cost rise can also be imported by ethanol, which must be accounted for in industrial production.

In this prepolymerization process, water concentration should be high enough for smoothly stirring, and meanwhile as a byproduct of amidation, water should not be added too much to hinder polymerization equilibrium shifts. Water concentration was controlled to be 29 wt % in the initial stage of prepolymerization and 10 wt % in the final stage. Diamines, dicarboxylic acids, water, and prepolymers would finally form a slurry in this process, phase state of which was critical for the successful proceeding of prepolymerization because the solid content in this system was so high that stirring and heat transmission were greatly affected by temperature, pressure, and equilibration time, which must be controlled carefully to avoid agitator stucking or discharge valve blocking.[33]

Molecular weight of stepwise polymerization products can be controlled conveniently by adjusting the stoichiometry of reactants and end capping agents. For PA10T, excess DA was usually added and commonly used end capping agent was benzoic acid (BA).[34-40]

The monofunctional monomer, often referred to as a molecular weight stabilizer, controls, and limits the polymerization of bifunctional monomers because the growing polymer yields chain ends devoid of functional groups and therefore incapable of further reaction. Thus, the use of benzoic acid in the polyamide synthesis yields a polyamide with phenyl end groups that are unreactive toward polymerization (Scheme 1).

In our prepolymerization system, a slight excess of 4 mol % of DA compared with TA was used. Prepolymerization was conducted at different concentrations of BA and finally polymers were obtained by SSP of prepolymers, which was conducted by a tumble dryer at a vacuum of 30 Pa. The results are shown in Table I.

Although excess DA was added into prepolymerization autoclave, concentration of amine groups of the prepolymers were not higher than that of acid groups, which was derived from DA loss during water discharge process obviously. In fact, pH of discharged water was about 12, and the pungent water was also concentrated by a rotary evaporator and the residual substance presented itself a similar ^{1}H-NMR spectra as DA. What was more, amine group decreased greatly after SSP and became

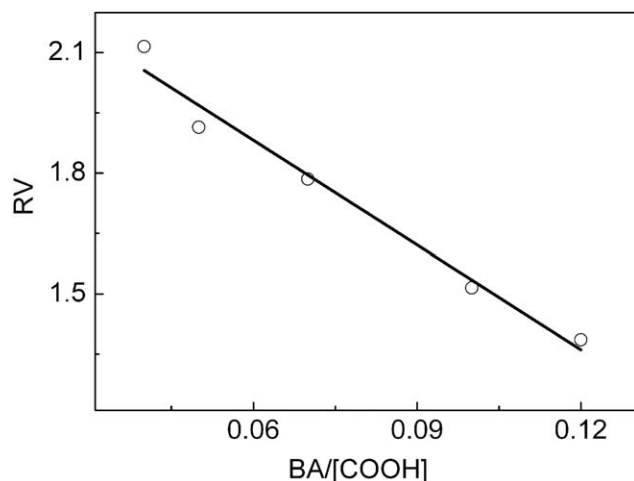**Figure 1.** Linear relation between RV of PA 10T and BA concentrations.

Figure 3. Rheological curves of PA10Ts with different BA concentrations.

much lower than acid group, which was also caused by DA loss at high vacuum and high temperature during SSP process.

Relative viscosity (RV) is a convenient parameter to characterize molecular weight of polymers and can be detected easily by Ubbelohde viscometer. RV decreased greatly with increasing of BA concentration and this trend can be found visually from Figure 1. RV decreases nearly linearly with BA concentrations, which gives direct proof of BA as a molecular weight stabilizer.[41]

^{13}C-NMR is a powerful tool to detect polymer terminal groups, from which contents of terminal groups can be quantified. The aromatic region of ^{13}C-NMR spectra of polyamides produced under different contents of BA was shown in Figure 2. Tx and Bx represent carbon atoms of terephthalic or benzoic acid end group, respectively. Peaks were assigned according to lit.[42,43]

Considering the low sensitivity of ^{13}C-NMR, terminal carboxylic acid group with higher concentration was chosen to be a reference to determine the concentration of phenyl groups deduced from benzoic acid. Terephthalic end groups (Tx) appeared at 133.27, 130.68, and 127.38 ppm, and benzoic end groups (Bx) appeared at 135.17, 133.83, 129.61, and 126.97 ppm. The ratio
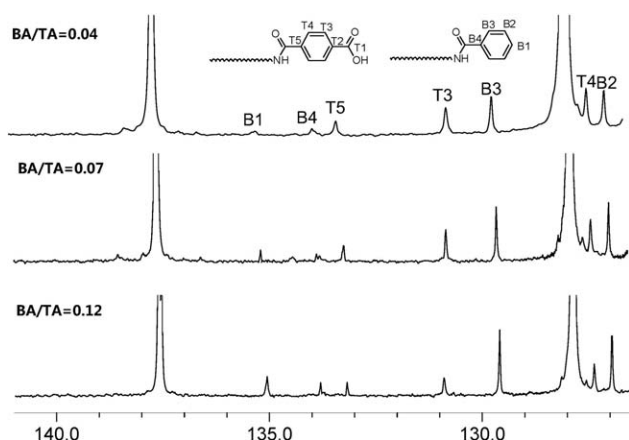
of B2 to T4 increased with increasing BA concentrations as shown in Figure 2, indicating that BA affects as a capping agent.

Capillary rheometer is an appropriate instrument to characterize materials' flow and deformation properties under conditions of high shear rate and at elevated temperatures. Rheological curves of PA10T with different RV can be found in Figure 3. With BA concentrations increasing, shear viscosity curves move down gradually, implying a decreasing of shear viscosity, which was derived from the decreasing molecular weight of the corresponding polyamides.

Fluidity Improvement of Semiaromatic Polyamides with Oligomers

The objective to produce PA10T oligomers is to improve fluidity of PA10T with normal molecular weight ($RV = 2.1$–2.5, and only in this range, mechanical properties of polyamides can be satisfied.) for high-end products applications. Hence PA10T oligomers were added into PA10T with relatively high molecular weight (Table I, run 1) as flow modifiers, the fluidity of which were compared with PA6T/66 counterparts. The result is shown in Figure 4. With only about 15 wt % of PA10T oligomer ($RV = 1.744$), the fluidity of PA10T mixture decreased significantly to the level of PA6T/66 counterparts. PA10T oligomer with lower RV (1.515) led to even more obvious fluidity improvement as can be seen.

Strickly speaking, prepolymers are oligomers with much lower molecular weight, usually lower than 1500 g/mol. Cost advantage of using prepolymers as flow modifiers in comparison with oligomers is remarkable in consideration of energy-intensive solid state polymerization. Therefore, prepolymers (Table I, run 2) were mixed with PA10T to improve its fluidity and the result is shown in Figure 5. Similar fluidity improvement can be achieved with about 1–3 wt % of prepolymers compared to 15 wt % oligomers.

In the next step, modified polyamides by adding TiO$_2$ and talc were produced to test other performances of oligomers and prepolymers engaged compounds to determine the final flow

Figure 2. ^{13}C-NMR spectra of polyamides produced under different contents of BA.
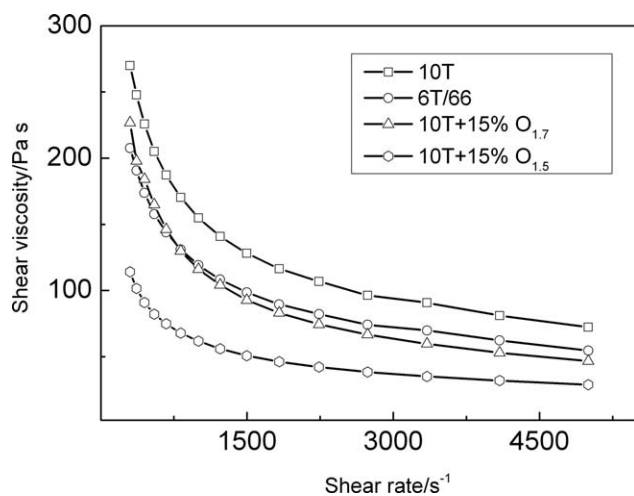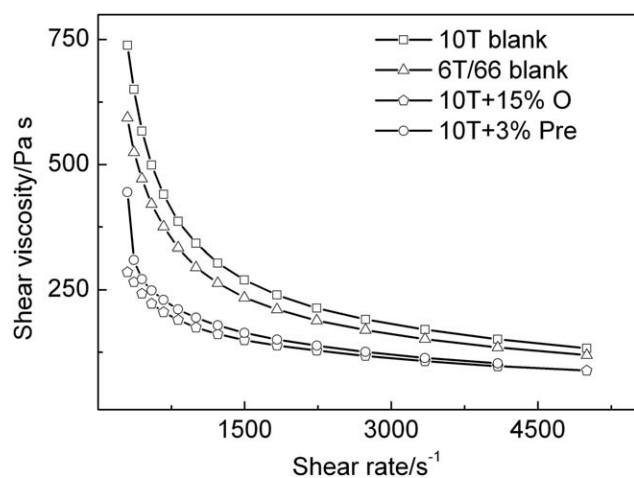
Figure 4. Fluidity comparisons of PA10T, PA6T/66 and PA10T oligomers mixtures.
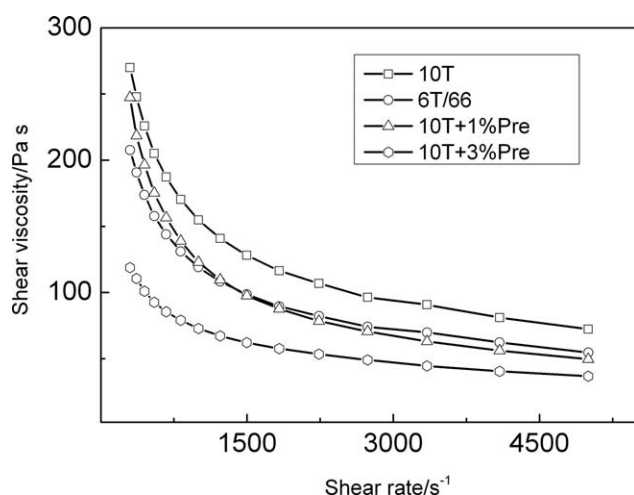
Figure 5. Fluidity comparisons of PA10T, PA6T/66 and PA10T prepolymers mixtures.

Figure 6. Fluidity comparisons of modified PA10T, PA6T/66 and PA10T compounds.

modifier for practical use and the results are shown in Table II and Figure 6. The high molecular weight PA10T is from Table I, run 1. The fluidity of the polyamide composition based on PA6T/66 is better than that of counterparts based on PA10T. However, after adding 15 wt % of oligomer, the fluidity of PA10T-based compounds increased remarkably and exceeds that of PA6T/66 counterparts. The comparable fluidity improvement can also be achieved by incorporation of 3 wt % prepolymer. Mechanical properties of modified polyamides were also tested. As can be seen from Table II, mechanical properties of sample 4 (PA10T+3 wt % prepolymer) decreased greatly compared with sample 1 (PA10T blank), while sample 3 (PA10T+15 wt % oligomer) decreased slightly. Hence, the oligomer with $RV = 1.515$ was an effective flow modifier to improve fluidity of PA10T and meanwhile maintains mechanical properties.

CONCLUSIONS

PA10Ts with varying molecular weight were synthesized by a two-step polymerization process through adding different amount of BA. Molecular weight as identified by RV decreased linearly with increasing BA concentrations. Fluidity behaviors of PA10Ts with varying molecular weight were tested and low RV PA10Ts were used as flow modifiers to improve fluidity of high molecular weight PA10T, leading to high fluidity polyamide compositions with fairly mechanical properties.

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