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STUDIES ON PHASE SEPARATION OF POLYESTERIMIDE-MODIFIED EPOXY RESINS. I. SYNTHESES AND PROPERTIES OF ORGANO-SOLUBLE POLYESTERIMIDES

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ABSTRACT

A series of polyesterimides based on aromatic bis(trimellitate) dianhydride in main chain were prepared by polycondensation of *t*-butyl-*p*-phenylenebis(trimellitate) dianhydride (BPBDA) and phenylene bis (trimellitate) dianhydride (PBDA) with benzidine and its derivates. The results show that the incorporation of noncoplanar structure led by introducing alkyl substituents on dianhydride and benzidine can improve the solubility of polyesterimides in organic solvents. It also displays that the introducing substituents lead to a decrease in glass transition temperature and influence the β relaxation of PEsI. By comparing the chemical structure and the dynamical mechanic date, we suggest that the β relaxation correspond to the motion involving the imide ring and phenylene groups of the diamine.

Key Words: Organo-soluble polyesterimides; Noncoplanar structure; Solubility; β relaxation

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INTRODUCTION

Epoxy resins are currently used for many important applications such as adhesives, encapsulates, and advanced composite matrixes. However, the further use of epoxy resins is limited because of their inherent brittleness. In recent years, the feasibility of toughening highly crosslinked networks with high modulus and high Tg thermoplastics has been investigated. In our previous work, a series of novel polyetherimides were synthesized and used to modify thermosetting resin, the modified resin displayed a toughening effect without sacrificing other important properties.[1–4]

Aromatic polyesterimides are increasingly used in aerospace and microelectronic industries because of their outstanding thermal stability, high mechanical strength, superior electrical/insulating properties, and excellent chemical stability.[5–10]

Since polyesterimides (PEsI) have higher Tg and higher modulus than those of polyetherimide, there is an attempt to use polyesterimides to modify epoxy resins and bismaleimide resins as tougheners in order to further improve the thermal stability and flexural modulus of modified epoxy resins. However, one of the disadvantages of these polymers is their limited solubility in most organic solvents. Recently, various kinds of polyimides have been synthesized, the overall goal of this ongoing research is to modify the structure of aromatic polyimides to attain solubility in common organic solvents without substantially decreasing the rigidity of their backbones. It has been reported that it can improve the solubility of aromatic polyimides by introducing out-of-plane constituents into the main chain of polyimides,[11] and their properties have reported in much of the literature. However, the research of the organo-soluble PEsI has been rarely reported. As the first step, the relationship between solubility and chemical structure of materials must be clarified so that these new polyesterimides could be used as potential toughners in thermosetting resins for a better toughening effect.

The objective of this research is to investigate the effect of introducing methyl groups in polyesterimide backbones through the synthesis and polymerization of appropriately substituted dianhydride. A series of polyesterimides (PEsI) based on aromatic bis(trimellitate) dianhydride were synthesized and the relationship between the solubility and the number of sidegroup substituents were investigated. The relationship between β relaxation behavior of polyesterimides and chemical structures with different diamines and dianhydrides were discussed.

EXPERIMENTAL

Materials

Pyridine was refluxed with CaH_2 for 3 h and distillated, as was benzene and N-methyl-2-pyrolidone. Trimellitic anhydride (TMA, MERCK-Schuchardt) was purified after refluxed and recrystallized in toluene and acetic anhydride (4:1 at volumn ratio) and then dried at 145°C in a vacuum oven. Benzidine (BZD), 3,3,5,5-tetramethyl benzidine (TMBZD) (Shanghai Third Reagent Factory) and o-tolidine (OTOL, Shanghai Research Institute of Synthetic Resin) were dried in vacuum oven before polymerization without further purification.

Measurements

The glass transition temperatures (T_g) of Polyesterimides were determined by a differential scanning calorimeter (SETARAM DSC 92) from room temperature to 350°C at a heating rate of 10°C/min under nitrogen.

The inherent viscosity of PEsI was obtained in the concentration of 0.5 g/dL at 30°C in N-methyl-2-pyrrolidone as solvent.

Dynamic mechanical analysis was carried out with a NETZSCH DMA 242 apparatus at a heat rating of $5°C\,min^{-1}$ from room temperature to 300°C. The specimens used were about 0.05 mm thick and were prepared as follows: The solution of Poly(amic acid) in NMP was coated onto glass substrates (25.5 mm × 75.5 mm) and prebaked at 80°C for 1 h, then the films were heated up to 200°C and kept at 200°C for 5 h. in a vacuum oven.

Thermogravimetric analysis was carried out with a Pyris 1 TGA at a heating rate of $10°C\,min^{-1}$ from room temperature to 500°C. The temperature of 5% weight loss were recorded.

FTIR spectra were recorded with a Nicolet Magna-IR 550.

Monomer Synthesis

t-Butyl-*p*-dioxybenzene Bisesteranhydride (BPBDA)

t-butyl-*p*-dioxybenzene bisesteranhydride was synthesized as follows: 96.0 g of TMA (0.5 mol) was dissolved in 250 mL of thionyl chloride in a three-necked 500 mL round-bottomed flask equipped with a stirrer. After refluxing for 2 h., the thionyl chloride was removed by reduced pressure distillation. When the solution in the flask was cooled to 50°C, 10 mL (0.124 mol) of pyridine and 60 mL of benzene were added. After a while, 41.6 g of *t*-butyl-*p*-dioxybenzene (0.25 mol) was dissolved in 150 mL of pyridine, and the solution was added dropwise to the three-necked round-bottomed flask with vigorous stirring under a nitrogen atmosphere at 50°C for 1 h. Then the flask was heated to 90°C for 3 h and filtrated to remove pyridinium while it was hot. The filtrate was distilled to remove the solvent, and crystals were obtained. The crystals were refluxed and recrystallized in the solution mixed of toluene and acetic anhydride (4:1 at volume ratio). The melting point of BPBDA is 218°C and the yield is 81%. ^1H NMR ($CDCl_3$): $\delta(ppm) = 1.35$ (s, 9H, $-CH_3$); 7.08–7.24 (m, 3H, aromatic); 8.12–8.20 (m, 2H, aromatic), 8.68–8.74 (m, 2H, aromatic); 8.78 (s, 2H, aromatic) IR (KBr): 1867 cm^{-1}, 1783 cm^{-1} (imide C=O); 1738 cm^{-1}(ester C=O), 1483 cm^{-1} (phenyl ring), 1238 cm^{-1} (ester C–O).

Phenylene-bis(trimellitate) Dianhydride(PBDA)

Phenylene-bis(trimellitate) dianhydride was synthesized as follows: 55 g of TMA (0.2865 mol) was dissolved in 120 mL of thionyl chloride in a 250 mL three-necked round-bottomed flask equipped with stirrer. After refluxing for 2 h, the thionyl chloride was removed by reduced pressure distillation. The solution in the flask was first cooled to 50°C, then 35 mL of pyridine and 100 mL of benzene were added. After that, 15.8 g of 1,4-benzenediol (0.1425 mol) was dissolved in 100 mL of pyridine, and the solution was added dropwise to the three-necked round-bottomed flask with vigorous stirring under a nitrogen atmosphere at 50°C for 1 h. Then the flask was heated to 90°C for 3 h and filtrated to remove pyridinium while it was hot. The filtrate was distilled to remove the solvent and crystals were obtained. The crystals were refluxed and recrystallized in the solution mixed of toluene and acetic anhydride (4:1 at volume ratio). The melting point of PBDA is 275°C and the yield is 78%. ^{1}H-NMR (DMSO): δ(ppm) = 7.47–7.53 (m, 4H, aromatic); 7.84–7.88 (m, 2H, aromatic); 8.33–8.35 (m, 2H, aromatic); 8.42 (s, 2H, aromatic). IR (KBr): 1867 cm^{-1}, 1783 cm^{-1} (imide C=O), 1738 cm^{-1} (ester C=O), 1483 cm^{-1}(phenyl ring), 1238 cm^{-1} (ester C(O).

Polyesterimide Synthesis

Diamine was dissolved in N-methyl-2-pyrolidone, then bisesteranhydride was added at the stoichiometric ratio of diamine. The mixture was stirred at room temperature under a nitrogen atmosphere for 8 h and Poly(amic acid) (PAA) was obtained. The solution was then precipitated into ethanol, and the sedimentary polymer (PAA) obtained through filtration was converted to the corresponding polyesterimide by heating at 200°C in a vacuum oven for 5 h. The yield of PEsI is about 97%.

RESULT AND DISCUSSION

The chemical structure of PEsI is shown in Fig. 1.

Table 1 displays that the solubility of polyesterimides in organic solvents was related to the number of introducing methyl substituents on biphenyl backbone. The PEsI based on TMBZD has the best solubility due to the noncoplanar structure of the imide unit, while the one based on BZD is insoluble in familiar organic solvents. It can also be seen that the alkyl groups

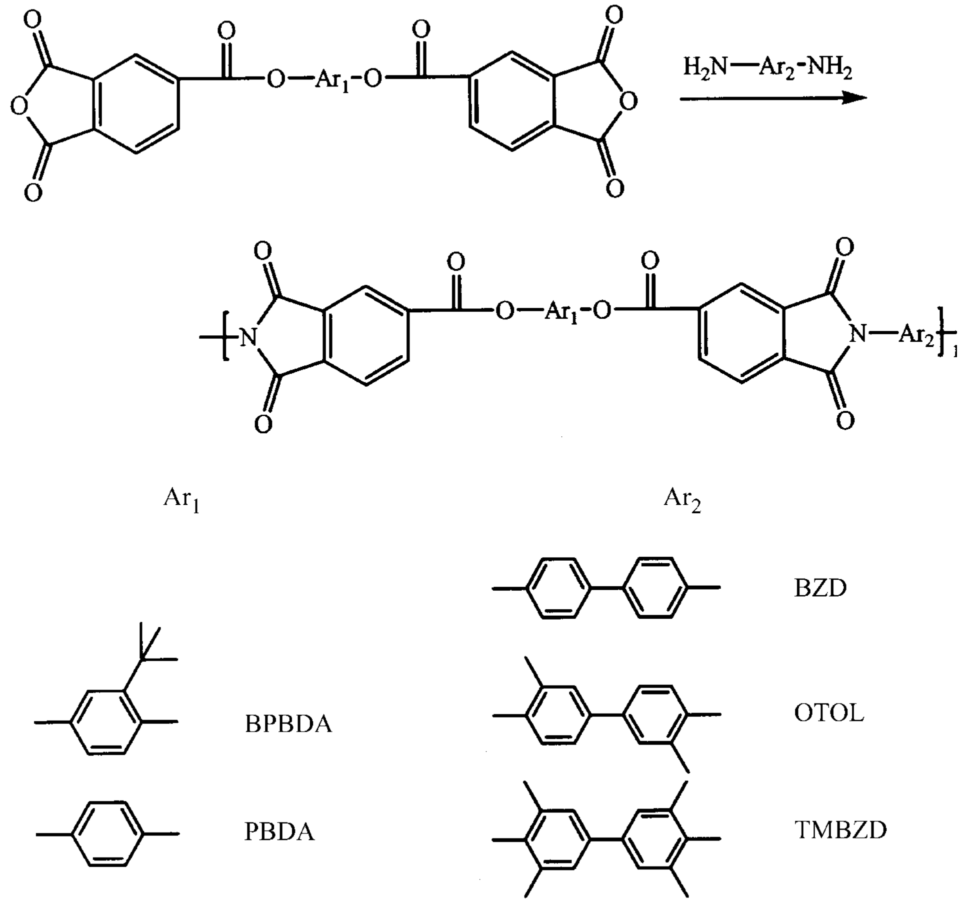

Figure 1. Chemical structure of polyesterimides.

on dianhydride can improve the solubility, the PEsI based on BPBDA has better solubility than the corresponding ones based on PBDA.

As illustrated in Table 1, the glass transition temperature decreases with the increasing methyl substituents on main chains among the polyesterimides based on BPBDA and benzidine and their derivates. Furthermore, the glass transition temperature of PEsI synthesized from PBDA is higher than that of the PEsI containing BPBDA. TGA data also shows that PEsI based on PBDA has better thermal performance.

It was found that the PEsI based on PBDA and benzidine was insoluble in NMP and its film coated on glass was brittle, which is different from Loncrini's result,[6] which reported that the PEsI is soluble in NMP and its film is flexible. The difference might be caused by the degree of imidization.

From computer modeling, the bond rotation angle ω' between imide ring and phenylene ring is calculated. It is shown that the dihedral angle between these two rings is less than 10 degrees in PEsI based on BZD,

Table 1. T_g, TGA Data and Solubility of PEsI in Organic Solvents

THF	NmP		m-Cresol		[η]* (0.5 g/dL)	T_g (°C)	Film	TGA Data 5% Wt. Loss Temperature (°C)
BPBDA-BZD*	i s	i s	i s	p s	0.42	274	Flexible	405
BPBDA-OTOL	p s	i s	s	s	2.04	265	Flexible	392
BPBDA-TMBZD	s	p s	s	s	0.49	249	Brittle	383
PBDA-BZD*	i s	i s	i s	i s	0.23	309	Brittle	413
PBDA-OTOL*	i s	i s	i s	p s	0.25	309	Brittle	408
PBDA-TMBZD	p s	p s	s	s	0.50	306	Brittle	466

[η] of PEsI was determined in N-methyl-2-pyrolidone at 30°C.

*For PEsI is insoluble in N-methyl-2-pyrolidone, [η] of poly(amic acid) was determined in N-methyl-2-pyrolidone at 30°C.

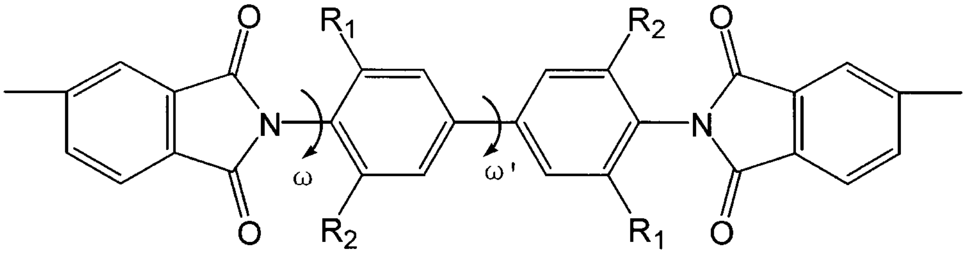

Figure 2. Schematic diagram of bond rotation of PEsI.

the dihedral angle ω increases with the number of methyl substituents on BZD, while the dihedral angle ω′ between phenylene rings does not change. The chemical structure and bond rotation angle of BZD, OTOL and TMBZD are shown in Fig. 2 and Table 2. The introducing substitute groups result in an increase in the dihedral angle ω between the imide ring and phenylene ring. The coplanar structure is broken because the bond rotation weakens the conjugation of the main chain. The introducing tertiary butyl on anhydride enhances the distance between the polyesterimide chains and

Table 2. Bond Rotation Degree of PEsI

Diamine	ω	ω′
BZD (R_1=R_2=H)	9°	37°
OTOL (R_1=CH_3 R_2=H)	38°	36°
TMBZD (R_1=R_2=CH_3)	53°	33°

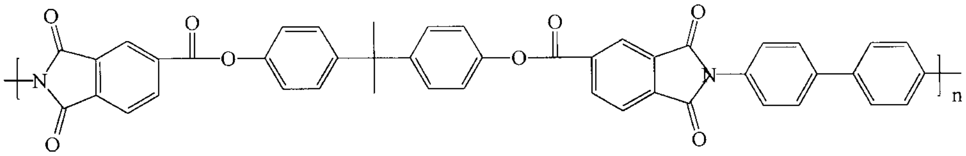

Figure 3. Chemical structure of BTPDA-BZD.

affects the stack of the molecules, which influences the solubility of PEsI and leads to a decrease in glass transition temperature.

Dynamic mechanical data of BPBDA-BZD and BPBDA-OTOL are given in Figs. 3 and 4. To clarify the relationship between dynamic mechanical behavior and chemical structure, a specimen of BTPDA-BZD, which was synthesized from 2,2-bis(p-trimellitoxyphenyl)propane dianhydride (BTPDA) and benzidine,[6] was used to compare with the newly synthesized PEsI films. The chemical structure of BTPDA-BZD is listed in Fig. 3:

Figures 4 and 5 show dynamic mechanical behavior of PEsI films. In the temperature range from 30 to 300°C, it is clear that both the loss factor (tan δ) and the loss modulus (E″) exist two relaxation processes (α and β relaxations).

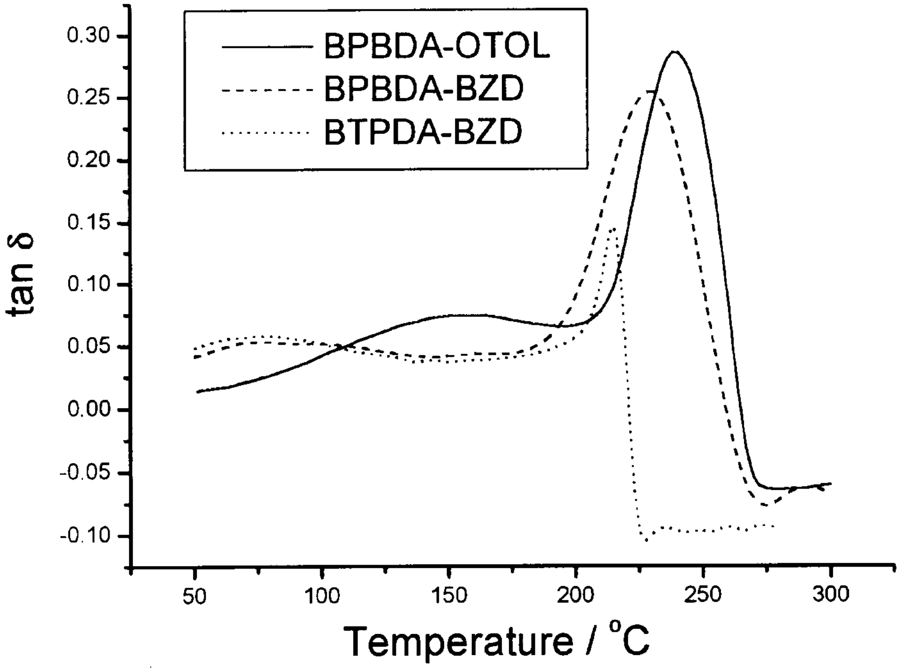

Figure 4. Dynamic tan δ data for different PEsI at 1.0 Hz. Temperature range 50–300°C.

The α relaxation of PEsI, corresponding to the glass transition temperature, occurs at different temperatures, respectively. The experiments show that the β relaxation is not affected by cyclic thermal treatment, which means that the β relaxation is not due to the loss of solvent. A similar β relaxation was found in BTPDA-BZD and BPBDA-BZD, no significant change in β relaxation temperatures and relaxation strength between the two samples can be observed. The β relaxation temperature of BTPDA-BZD is about 75°C, while that of BPBDA-BZD is 77°C. This indicates that the structure of dianhydride does not affect the β relaxation process although BPBDA has significantly increased the chain rigidity of PEsI with a higher extent of conjugation.

Some reports indicate that the β relaxation process is associated with socalled rotational vibrations of the phenylene rings.[12,13] In this work, from the results of Table 2 there is no obvious difference in ω′ among the PEsI, therefore, it is reasonable to consider the β relaxation is related to the bond rotation of ω.

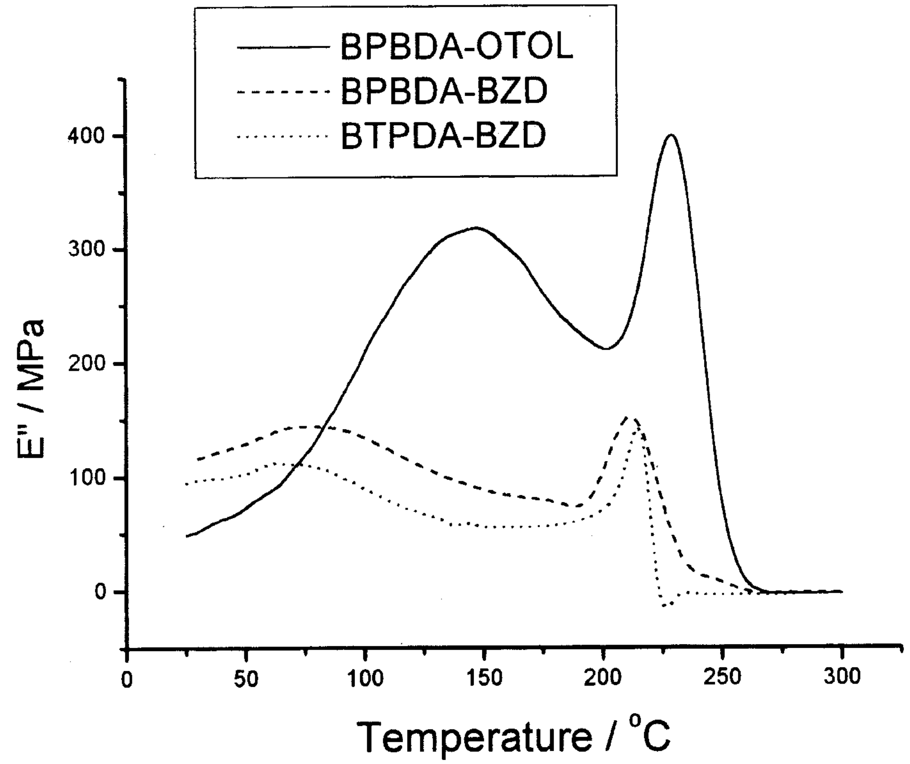

Figure 5. Dynamic mechanical data for different PEsI at 1.0 Hz. Temperature range 50–300°C.

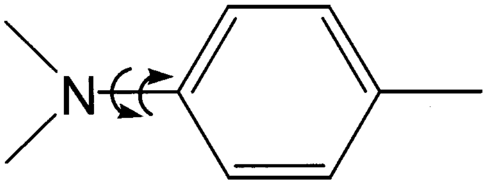

Figure 6. Schematics of the motion involving the imide ring and phenylene groups.

The results also suggest that the β relaxation process is associated with the motion involving the imide ring and phenylene groups of the diamine, as suggest in Fig. 6.

As shown in Fig. 4, the position of β relaxation maximum of BPBDA-OTOL shifts to the higher-temperature region compared with BPBDA-BZD. The β relaxation temperature of BPBDA-OTOL is about 145°C, much higher than that of BPBDA-BZD, and the relaxation strength is also much stronger. This reveals that the relative strong $\tan\delta$ is attributed mainly to the introducing methyl groups on benzidine. Because of the steric hindrance effect caused by the methyl substitute groups, the biphenyl group can not rotate freely around the "hinges", more energy is required to overcome the steric hindrance effect, so that the position of β relaxation is shifted to higher temperature.

The primary experiments show that some of the polyesterimides can be dissolved in bismaleimide (BMI) resins and epoxy resins, meanwhile, the morphology of co-continuous and phase inversion were observed by controlling the process of phase separation. The detailed work is underway.

CONCLUSION

The introducing alkyl substitute groups on dianhydride and benzidine moiety improve the solubility of the polyesterimide due to the noncoplanar structure of the imide unit. The methyl substitute groups on benzidine will increase the dihedral angle between the imide ring and phenylene ring, which weakens the conjugation of the polyesterimide backbones. Dynamical mechanical data show that the β relaxtion of PEsI is related to the structure of the diamines, the position of β relaxation maximum shift to the higher-temperature because of the bond rotation limitation, which is caused by the steric hindrance effect due to the introducing methyl substitute groups.

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REFERENCES

1. Yu, Y.F.; Cui, J.; Chen, W.J.; Li, S.J. Journ. Mac. Sci. Chem. **1998**, *A35* (1), 121.
2. Cui, J.; Yu, Y.F.; Li, S.J. Journ. Mac. Sci. Chem. **1998**, *A35* (4), 649.
3. Jing, J.Y.; Cui, J. et al., Macromol. Chem. Phys. **1999**, *200*, 1956.
4. Luo, Y.; Li, H.; Li, S.J. Journ. Mac. Sci., Part A, **2001**, *A38* (11), 1019.
5. Sroog, C.E.; Endrey, A.L.; Abramo, S.V.; Berr, C.E.; Edwards, W.M.; Oliver, K.L. J. Polym. Sci., Part A, **1965**, *3*, 1373.
6. Loncrini, D.F. J. Polym. Sci., Part A-1, **1966**, *4*, 1531.
7. Sroog, C.E. J. Polym. Sci. Macromol. Rev. **1976**, *11*, 161.
8. Kricheldorf, H.R.; Schwarz, G.; Berghahn, M. Macromolecules **1994**, *27*, 2540.
9. Kricheldorf, H.R.; Pakull, R. Macromolecules **1998**, *21*, 551.
10. Pyo, S.M.; Kim, S.I. et al., J. Polym. Sci., Part A. Polymer Chemistry, **1999**, *37*, 937.
11. Lin, S.H.; Li, F.M.; Cheng, S.Z.D.; Harris, F.W. Macromolecules **1998**, *31* (7) 2080.
12. Butta, E.; De Petris, S.; Pasquoni, M. J. Appl. Polym. Sci. **1969**, *13*, 1073.
13. Perena, J.M. Die Makromol. Chem. **1982**, *196*, 61.

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