Polymer Journal, Vol. 26, No. 6, pp 722—727 (1994)

Preparation and Properties of New Polyarylates from 2,2′-Bis(*p*-carboxyphenoxy)biphenyl or 2,2′-Bis(*p*-carboxyphenoxy)-1,1′-binaphthyl and Various Bisphenols

Guey-Sheng LIOU, Masa-aki KAKIMOTO, and Yoshio IMAI*

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan.

(Received November 22, 1993)

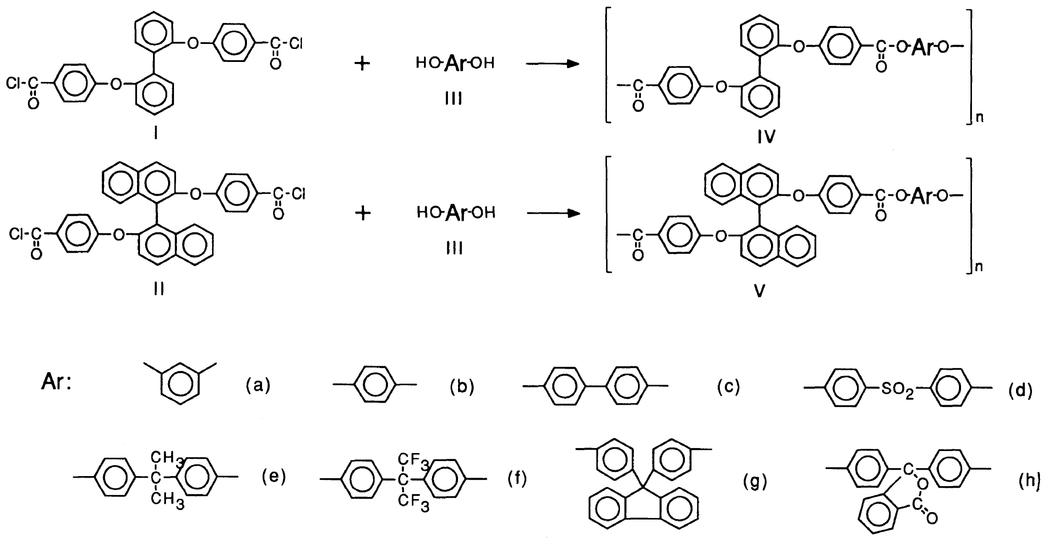
ABSTRACT: New biphenyl-2,2′-diyl and 1,1′-binaphthyl-2,2′-diyl-containing polyarylates having inherent viscosities up to 1.02 dl g^{-1} were synthesized by the phase-transfer catalyzed two-phase polycondensation from the diacid chlorides of 2,2′-bis(*p*-carboxyphenoxy)biphenyl or 2,2′-bis(*p*-carboxyphenoxy)-1,1′-binaphthyl and various bisphenols. These polyarylates were readily soluble in a variety of organic solvents including *N*-methyl-2-pyrrolidone, *m*-cresol, pyridine, and chloroform. These polymers containing biphenyl and binaphthyl units had glass transition temperatures in the range of 144—200°C and 215—268°C, respectively. They began to lose weight at around 400°C, with 10% weight loss being recorded at about 450°C in air.

KEY WORDS 2,2′-Bis(*p*-carboxyphenoxy)biphenyl / 2,2′-Bis(*p*-carboxyphenoxy)-1,1′-binaphthyl / Polyarylates / Solubility /Thermal Behavior /

Interest in molecular engineering of physical properties for high-performance polymers persists because small alteration of the molecular structure of a polymer can dramatically influence performance and processing properties. Generally, alteration of high-performance polymers focuses on changes in substitution pattern of aromatic cyclic units comprising the bulk of such polymers. Change in chain stiffness or rigidity *via* modification of primary and secondary structures is particularly effective.[1] It is well known that wholly aromatic polyesters (polyarylates) possess high thermal stability and excellent mechanical properties.[2] There are numerous examples in the literature of use of biphenyl-4,4′-diyl or 1,1′-binaphthyl-4,4′-diyl units to promote liquid crystallinity in polyesters.[3-6] However, the high melting temperatures or softening temperatures and limited solubility in organic solvents of most polyarylates make their processing into articles difficult unless flexible spacers are included in the systems, thereby lowering the thermal stability. One of the approaches to improve their processability with simultaneous preservation of thermal stability would be the introduction of bulky, kinked, and cranked biphenyl-2,2′-diyl and 1,1′-binaphthyl-2,2′-diyl units into the polymer backbone. Recently, we have reported that the 1,1′-binaphthyl-2,2′-diyl-containing polyarylates derived from 2,2′-dihydroxy-1,1′-binaphthyl and various aromatic diacid chlorides had higher glass transition temperatures (T_g) by about 50°C and better solubility than the biphenyl-2,2′-diyl-containing polyarylates.[7,8] Our recent studies also revealed that highly kinked and cranked aromatic diacid chlorides of 2,2′-bis(*p*-carboxyphenoxy)biphenyl (BBCA) and 2,2′-bis(*p*-carboxyphenoxy)-1,1′-binaphthyl (BNCA) were effectively used to prepare novel soluble aromatic polyamides through the polyconden-

---

* To whom correspondence should be addressed.



Scheme 1.

sation with aromatic diamines.[9] Therefore, the diacid chlorides of BBCA and BNCA would be potential monomers for producing soluble polyarylates with retention of high thermal stability.

This article deals with the preparation and characterization of new soluble polyarylates containing the kinked and cranked biphenyl-2,2′-diyl and 1,1′-binaphthyl-2,2′-diyl units by phase-transfer catalyzed two-phase polycondensation of the diacid chlorides with various bisphenols (Scheme 1). The characteristics of polyarylates such as solubility and thermal behavior are also discussed.

EXPERIMENTAL

Materials

2,2′-Bis(*p*-carboxyphenoxy)biphenyl (BBCA) and 2,2′-bis(*p*-carboxyphenoxy)-1,1′-binaphthyl (BNCA) were prepared by the condensation of *p*-fluorobenzonitrile with biphenyl-2,2′-diol and 2,2′-dihydroxy-1,1′-binaphthyl, respectively, followed by the hydrolysis reaction of the dinitrile compounds in potassium hydroxide solution, according to the previously reported procedures.[9] The reaction of dicarboxylic acids BBCA and BNCA with thionyl chloride in the presence of a few drops of dimethylformamide (DMF) as a catalyst afforded diacid chlorides **I** and **II**, respectively. Diacid chloride **I** was purified by sublimation to give white needles; mp 130—131 °C (lit.[9] 130—131 °C). Diacid chloride **II** was purified by recrystallization from a mixture of hexane and benzene to afford pale yellow crystalline powder; mp 180—181°C (lit.[9] 181—182 °C).

Various bisphenols were obtained commercially and purified by recrystallization. They included resorcinol (**IIIa**), hydroquinone (**IIIb**), biphenyl-4,4′-diol (**IIIc**), 4,4′-bis(4-hydroxyphenyl) sulfone (bisphenol S, **IIId**), 2,2-bis(4-hydroxyphenyl)propane (bisphenol A, **IIIe**), 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane (bisphenol AF, **IIIf**), 9,9-bis(4-hydroxyphenyl)fluorene (fluorene bisphenol, **IIIg**), and phenolphthalein (**IIIh**).

Benzyltriethylammonium chloride (BTEAC) was used as received. All the solvents employed were purified by distillation before use.

Polymerization

*Polymer **IVe** from **I** and **IIIe** by Two-Phase Method.* In a flask were placed 0.571 g (2.50

mmol) of **IIIe**, 15 mg of BTEAC, and 5.1 ml of 1 M aqueous sodium hydroxide. To the stirred solution was added quickly a solution of 1.158 g (2.50 mmol) of **I** in 5.0 ml of dichloromethane, and an additional 2.0 ml of the solvent used to rinse the residue of **I**. The two-phase mixture was vigorously stirred at 20 °C for 2 h. The reaction mixture was poured into 300 ml of hot water containing a small amount of hydrochloric acid. The precipitated polymer was collected by filtration, washed thoroughly with hot methanol, and dried 100°C under vacuum. The polymer weighed 1.54 g (99%) and had an inherent viscosity of 1.02 dl g^{-1}, measured at a concentration of 0.5 g dl^{-1} in *o*-chlorophenol at 30°C. The IR spectrum (film) exhibited an absorption at 1745 cm^{-1} (C=O).

Anal. Calcd for $(C_{41}H_{30}O_6)_n$: C, 79.59%; H, 4.89%. Found: C, 79.15%; H, 4.79%.

The other polyarylates were synthesized by similar procedure.

Measurements

IR spectra were recorded on a JASCO FTIR-5000 spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed with Shimadzu thermal analyzers DSC-41M and TGA-40M, respectively. Wide angle X-ray diffraction patterns were obtained at room temperature on a Rigakudenki RU-200 apparatus with nickel-filtered Cu-K_α radiation (50 kV, 180 mA). Weight-average molecular weight ($\bar{M}_w$) and number-average molecular weight ($\bar{M}_n$) were determined by means of gel permeation chromatography (GPC) on the basis of polyoxyethylene calibration on a JASCO apparatus (eluent, *N*,*N*-dimethylformamide (DMF)). Tensile properties were determined from stress–strain curves obtained with a Toyo Baldwin Tensilon UTM-II-20, and the measurements were performed at room temperature using solution-cast film specimens (about 0.1 mm thick, 1.0 cm wide, and 5.0 cm gauge length) at an elongation rate of 20% min^{-1}.

RESULTS AND DISCUSSION

Polymer Synthesis

The phase-transfer catalyzed two-phase polycondensation of aromatic dicarboxylic acid chlorides with bisphenols in the presence of BTEAC as a phase transfer agent is a convenient method for the preparation of polyarylates on a laboratory scale.[10] New biphenyl-2,2′-diyl- and 1,1′-binaphthyl-2,2′-diyl-containing Polyarylates **IVa**—**IVh** and **Va**—**Vh** were synthesized by the two-phase polycondensation starting from diacid chlorides **I** and **II**, respectively, with bisphenols **IIIa**—**IIIh**, and the results are summarized in Table I.

The polyarylates thus obtained had inherent viscosities of 0.15—1.02 dlg^{-1}, and the GPC curves of polyarylates indicated that the $\bar{M}_w$ values were 24000—390000 relative to standard polyoxyethylene, and the $\bar{M}_w/\bar{M}_n$ values, a measure of molecular weight distribution, were 1.5—1.7 (Table I). In more detail, the molecular weight values of the biphenyl-2,2′-diyl-containing polyarylates **IV** derived from diacid chloride **I** were generally much higher than those of the 1,1′-binaphthyl-2,2′-diyl-bearing polymers **V** from diacid chloride **II**. Since diacid chloride **II** have already been used for the synthesis of aromatic polyamides having enough high molecular weights as reported previously,[9] it is unlikely that the formation of binaphthyl series polyarylates **V** with rather low molecular weights is attributable to the lower purity of diacid chloride **II** compared with **I**. Therefore, the reason for the results remains unapparent. The formation of these new polyarylates was confirmed by means of IR spectroscopy and elemental analysis. The elemental analysis values of the polyarylates were in good agreement with the calculated values for the proposed structures.

Polymer Characterization

Table II shows the solubility behavior of the polyarylates. All the polyarylates except

Table I. Synthesis of polyarylates

Monomers[a]		Polymer				
Diacid chloride	Bisphenol	Code	η_{inh}[b] / $dl\,g^{-1}$	M_n[c] / $\times 10^4$	M_w[c] / $\times 10^4$	M_w/M_n[c]
I	**IIIa**	**IVa**	0.31	3.4	5.1	1.5
I	**IIIb**	**IVb**	0.18	—	—	—
I	**IIIc**	**IVc**	0.26	—	—	—
I	**IIId**	**IVd**	0.42	4.8	8.1	1.7
I	**IIIe**	**IVe**	1.02	26.2	39.0	1.5
I	**IIIf**	**IVf**	0.59	5.0	8.5	1.7
I	**IIIg**	**IVg**	0.48	5.9	9.5	1.6
I	**IIIh**	**IVh**	0.51	7.5	11.0	1.5
II	**IIIa**	**Va**	0.15	1.6	2.6	1.6
II	**IIIb**	**Vb**	0.16	1.4	2.4	1.7
II	**IIIc**	**Vc**	0.15	1.8	2.9	1.7
II	**IIId**	**Vd**	0.20	2.0	3.0	1.5
II	**IIIe**	**Ve**	0.33	5.2	8.0	1.5
II	**IIIf**	**Vf**	0.28	2.6	3.9	1.5
II	**IIIg**	**Vg**	0.30	2.8	4.8	1.7
II	**IIIh**	**Vh**	0.33	3.3	4.9	1.5

[a] Polymerization was carried out with 2.5 mmol of the bisphenol in 5.1 ml of 1 M aqueous sodium hydroxide and 2.5 mmol of the diacid chloride in 7.0 ml of dichloromethane in the presence of 15 mg of BTEAC at 20°C for 2 h.

[b] Measured at a concentration of $0.5\,g\,dl^{-1}$ in *o*-chlorophenol at 30°C.

[c] Determined by GPC on the basis of polyoxyethylene calibration.

Table II. Solubility of polyarylates[a]

Solvent	Polymer				
	IVa, IVd—IVh	**IVb**	**IVc**	**Va, Vd—Vh**	**Vb, Vc**
N-Methyl-2-pyrrolidone	+ +	+	+	+ +	+ +
Dimethylformamide	+ +	+	−	+ +	+ +
o-Chlorophenol	+ +	+ +	+	+ +	+ +
m-Cresol	+ +	+	+	+ +	+ +
Nitrobenzene	+ +	+	+	+ +	+ +
Pyridine	+ +	+	−	+ +	+ +
1,4-Dioxane	+ +	+	−	+ +	+ +
Tetrahydrofuran	+ +	−	−	+ +	−
Chloroform	+ +	−	−	+ +	+ +
Methanol	−	−	−	−	−
Acetone	−	−	−	−	−

[a] + +, soluble at room temperature; +, soluble or swelling on heating, −, insoluble.

polymers **IVb** and **IVc** were highly soluble in polar solvents such as *N*-methyl-2-pyrrolidone, *o*-chlorophenol, and *m*-cresol, and even in less polar pyridine and chloroform. Thus, the solubility of polyarylates is greatly improved by the introduction of the bulky, kinked, and cranked bipheny-2,2′-diyl and 1,1′-binaphthyl-2,2′-diyl units into the polymer backbone. The solubility studies also revealed that polyarylates **V** had better solubility than polyarylates

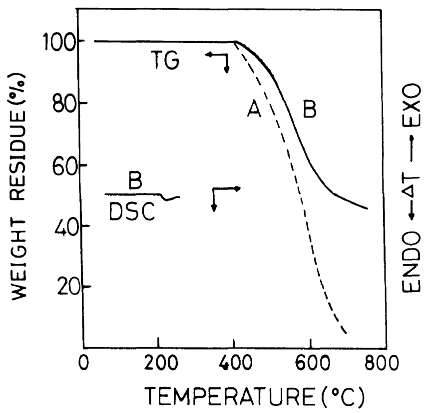


Figure 1. DSC and TG curves for polyarylate **Ve** in air (A) and in nitrogen (B). DSC heating rate = 20°C min^{-1} and TG heating rate = 10°C min^{-1}.

Table III. Thermal Behavior of Polyarylates

Polymer	T_g[a]	T_d[b]		T_{10}[b]	
		In air	In nitrogen	In air	In nitrogen
	°C	°C	°C	°C	°C
IVa	144	405	405	475	475
IVb	150	410	410	470	480
IVc	—	405	410	480	500
IVd	182	410	410	470	480
IVe	172	390	430	450	490
IVf	168	400	420	485	495
IVg	200	400	400	495	495
IVh	190	400	400	450	460
Va	215	400	405	460	480
Vb	220	400	405	470	480
Vc	245	400	410	465	480
Vd	230	390	400	450	460
Ve	230	410	420	480	485
Vf	220	400	405	470	480
Vg	262	400	405	470	485
Vh	268	410	410	475	490

[a] Determined by DSC at a heating rate of 20°C min^{-1} in nitrogen.

[b] T_d and T_{10} are temperatures of initial and 10% weight loss, respectively, measured by TG at a heating rate of 10°C min^{-1}.

IV in many organic solvents, where the bulky effect of binaphthyl structure is greater than that of the biphenyl. The better solubility of polyarylates **V** is in part due to their lower molecular weight. Polymer **IVe** could be cast into transparent and flexible film from the chloroform solution.

The X-ray diffraction studies revealed that polyarylates **IVb** and **IVc** were semicrystalline, whereas all of the other polymers were amorphous. Thus, the amorphous nature of these polymers was reflected in their excellent solubility, and this could be attributed to the introduction of bulky and unsymmetrical biphenyl-2,2′-diyl or 1,1′-binaphthyl-2,2′-diyl unit along the polymer backbone.

The thermal behavior of the polymers was evaluated by means of DSC and TG. The DSC and TG curves of the polyarylate **Ve** are given in Figure 1, and the glass transition temperatures (T_g) and decomposition temperatures (T_d) obtained are tabulated in Table III.

The T_gs of the biphenyl-2,2′-diyl- and 1,1′-binaphthyl-2,2′-diyl-containing polymers were in the range of 144—200°C and 215—268°C, respectively, and decreased with decreasing rigidity and symmetry of the polymer backbone, or with introduction of flexible linkages in the polymer main chain. The T_gs of polyarylates **V** derived from **II** were about 60°C higher than those of the corresponding polyarylates **IV** derived from **I** due to the difference of rigidity between binaphthyl and biphenyl units. The T_gs and solubility of polyarylates **IV** and **V** derived from the diacid chlorides of BBCA and BNCA with various bisphenols showed similar tendency with those of the polyarylates derived from both biphenyl-2,2′-diol and 2,2′-dihydroxy-1,1′-binaphthyl and aromatic diacid chlorides.[7,8]

All the polymers were stable up to 400°C in both air and nitrogen, and the temperatures of 10% weight loss were observed above 450°C on the TG curves in both atmospheres. There was no obvious difference in thermal stability between polyarylates **IV** and polyarylates **V**. In addition, the T_gs and decomposition temperatures of polyarylates **IV** and **V** also were very similar to the polyarylates derived from biphenyl-2,2′-diol and 2,2′-dihydroxy-1,1′-binaphthyl with aromatic dicarboxylic acid chlorides.[7,8]

The mechanical properties of the solution cast film of polyarylate **IVe** were measured. The tensile strength, elongation at break, and tensile modulus of the film were 73 MPa, 4.5%, and 2.0 GPa, respectively, while the other polymer films were too brittle to be measured due to not high inherent viscosities of these polymers.

CONCLUSIONS

The introduction of bulky, kinked and cranked 2,2′-biphenyl-diyl and 1,1′-binaphthyl-2,2′-diyl units into polyarylate backbones improved their solubility in various organic solvents. Polyarylates V derived from the diacid chloride of 2,2′-bis(*p*-carboxyphenoxy)-1,1′-binaphthyl had glass transition temperatures above 215°C, high thermal stability, and excellent solubility in various organic solvents, compared with those of polyarylates **IV** derived from 2,2′-bis(*p*-carboxyphenoxy)biphenyl. Thus, they are considered to be promising processable, high-perfomance plastics.

REFERENCES

1. H. H. Yang, "Aromatic High-Strength Fibers", Interscience, New York, N.Y., 1989.
2. Y. Imai and M. Kakimoto, "Handbook of Polymer Science and Technology, Vol. 1: Synthesis and Properties," N. P. Cheremisinoff, Ed., Dekker, New York, N.Y., 1989, p 177.
3. Z. Jedlinski and D. Sek, *J. Polym. Sci. Part A–1*, **7**, 2587 (1969).
4. D. Van Luyen and L. Strzeleck, *Eur. Polym. J.*, **16**, 303 (1980).
5. B. W. Jo and R. W. Lenz, *Makromol. Chem. Rapid Commun.*, **3**, 23 (1982).
6. T. D. Shaffer and V. Percek, *J. Polym. Sci., Polym. Lett. Ed.*, **23**, 185 (1985).
7. G. S. Liou, M. Kakimoto, and Y. Imai, *J. Polym. Sci., A, Polym. Chem.*, **30**, 2195 (1992).
8. G. S. Liou, M. Kakimoto, and Y. Imai, *J. Polym. Sci., A, Polym. Chem.*, **32**, 587 (1994).
9. G. S. Liou, M. Kakimoto, and Y. Imai, *J. Polym. Sci., A, Polym, Chem.*, **31**, 3265 (1993).
10. P. W. Morgan, "Condensation Polymers by Interfacial and Solution Methods", Interscience, New York, N.Y., 1965.