

One pot synthesis of high-molecule-weight polyetherimides and their copolymers from bis(chlorophthalimide) and dichlorodiphenylsulfone using diphenylsulfone as the solvent

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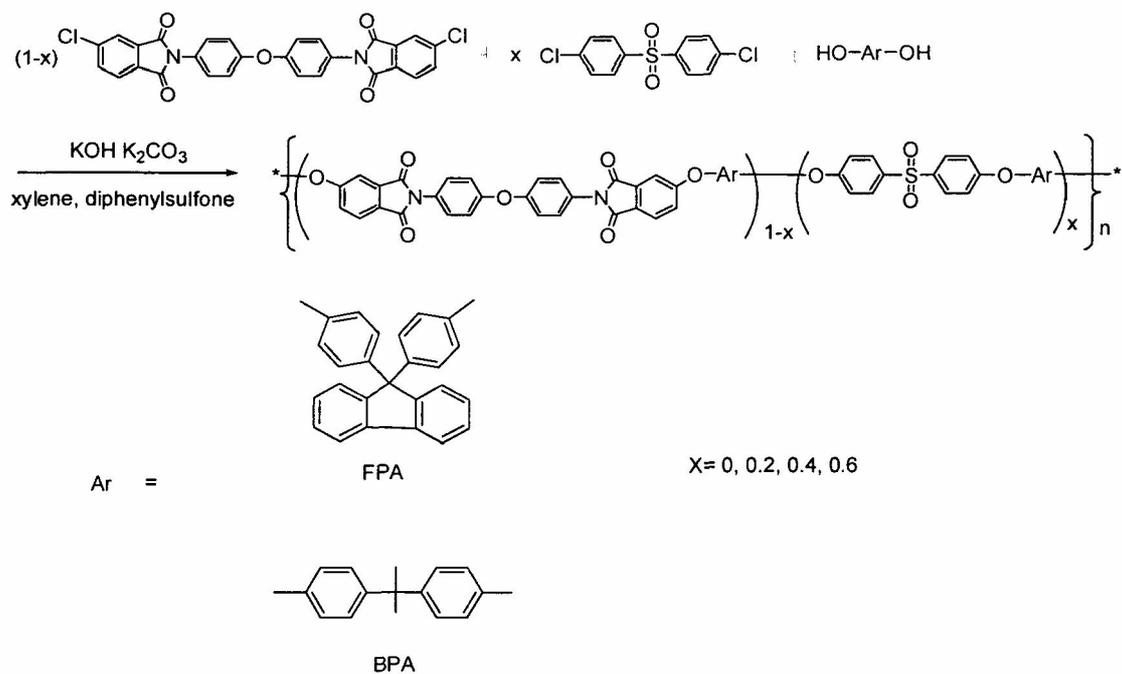
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High-molecule-weight polyetherimides and their copolymers have been synthesized in one pot from bis(chlorophthalimide), dichlorodiphenylsulfone and bisphenolate, which is contributed to using diphenylsulfone as the solvent. The inherent viscosities of polymers are range from 0.32 to 0.72 dl/g and their structures were confirmed by IR and elemental analyses. All of polymers have good solubility in common organic solvents. The 5% weight-loss temperatures of isomeric polyimides were 429-507⁰C in air. The glass-transition temperatures (T_g) of 4, 4'-(9-fluorenylidene) diphenol-based polymers are in the range of 204-268⁰C, and the T_g s increase as the ratios of diphenylsulfone increase. The glass-transition temperatures (T_g) of bisphenol A-based polymers are in the range of 198-204⁰C, while the T_g s unconspicuously change when the ratios of diphenylsulfone increase. Either 4, 4'-(9-fluorenylidene) diphenol or biphenol A is used, the mechanical properties of copolymers are the best when the ratio of diphenylsulfone is 20%. The wide-angle X-ray diffraction showed that all polymers are amorphous.

Polyetherimides which include additional ether functions, as the most important modified polyimides, have been receiving great attention as they may provide good processability owing to the presence of flexible ether links. GE's Ultem[®] and the Avimid[®] series which was pioneered by Du Pont are the most successful examples. Ultem[®] can be synthesized via the two-step method using dianhydrides and diamines, or by the nucleophilic displacement of bisphenolate and bis-chloro- or nitro phthalimides. The latter is more favorable because of its lower cost. However, it is difficult to get high-molecule-weight polymers because of the unstability of bisphthalimide in alkaline conditions. This reaction is usually carried out in aprotic solvents such as DMAc, DMSO, and NMP. However, it is difficult to get high-molecule-weight polymers because of the unstability of bisphthalimide in alkaline conditions. In this article, we synthesized poly(ether-imide-co-ether-sulfone) using diphenylsulfone as the solvent. Because of the immiscibility of diphenylsulfone with water, it is easy to get high-molecule-weight polymers. The properties of copolymers are also presented.



Scheme 1. Synthesis of poly(ether sulfone-co-ether imide)

The synthesis of polyimides via the nucleophilic displacement of bisphenolate and bis chloro- or nitro phthalimides could decrease the loss. The important chemistry is reported in a series of papers and patents by the researchers of GE Co.. In 1974 researchers in GE Co. reported the synthesis of PEI from biphenol and bis(chlorophthalimide), but the molecular weight was very low. In 1997 it was reported the synthesis of high-molecule-weight polyimides from bisphenol disodium that was prepared afore and bis(chlorophthalimide), however the yield of the synthesis of biphenol disodium was only 50%. In this paper, we successfully prepared high-molecule-weight polyimides and their copolymers from bis(chlorophthalimide) or diphenylsulfone and biphenol disodium synthesized in situ. We think that the use of diphenylsulfone as the solvent is critical to get high-molecule-weight polymers. Because of its immiscibility with water, the side reaction- the hydrolysis of bis(phthalimide) was inhibited even in the presence of excess potassium carbonate anhydrous. What's more, the solvent could be recovered because it will recrystallize from acetone. The inherent viscosities, yields, and elemental analyses of polymers are shown in Table 1. As shown in it, all of polymers had high molecular weight. We also found that the molecular weight of polymers from 4, 4'-(9-fluorenylidene) diphenol is higher than that of polymers from bisphenol A, which is contributed to the better solubility of the disodium of 4, 4'-(9-fluorenylidene) diphenol in diphenylsulfone.

All of the copolymer powders have good solubility in organic phenols, polar aprotic

solvents such as NMP, DMAc, DMSO, THF, and even in CHCl₃ and TCE, except ODA-FPA-0 which was partly soluble in phenols and polar aprotic solvents. When FPA was used, the solubility of polymers was enhanced by copolymerization. However, when BPA was used, all of polymers have similar solubility. The thermal and mechanical properties of polymers were studied. The temperatures of 5% weight loss (T_{5%}) of polyimides in air are in the range from 429 °C to 507 °C. The results indicated that the thermaloxidative stability of polymers is obviously poorer than others when the ratio of dichlorophenylsulfone is 60%. The reason is that poly (ether sulfone) is not as stable as poly (ether imide) at elevated temperature.

Table 1. Preparation of polymers.

polymer	η_{inh}^a (dl/g)	Yield (%)
ODA-FPA-0	0.65	97
ODA-FPA-20	0.61	94
ODA-FPA-40	0.58	99
ODA-FPA-60	0.72	96
ODA-BPA-0	0.32	93
ODA-BPA-20	0.45	95
ODA-BPA-40	0.38	95
ODA-BPA-60	0.33	96

All of the polymer films were cast from the 10% (w/v) solutions in DMAc and dried at 80 °C/12h+ 250°C/3h. The film of ODA-FDA-O is tough, flexible, but not transparent. The film of ODA-BPA-0 is highly brittle because of its lower molecular weight. Others are tough, flexible and transparent. The tensile strengths of at break, the modulus, and the elongations at break of polymers are 67-124 MPa, 1.34-2.48 GPa, and 3.5-8.9%, respectively. When the content of dichlorophenylsulfone is 20%, the tensile strengths are highest. When the content of dichlorophenylsulfone is high, the tensile strengths decrease rapidly. As the modulus and elongations at break are concerned on, no obvious trend is observe. The original storage modulus of the FPA-based polymers ranged from 1.36 to 3.16GPa. Regarding the peak temperature in the tanδ curves as the glass transition temperature (T_g), the polymer ODA-FPA-0 exhibits a T_g at 204°C, ODA-FPA-20 at 253°C, ODA-FPA-40 at 256°C, and ODA-FPA-60 at 268°C. The T_gs of polymers increased as the content of dichlorodiphenylsulfone increased. Polymer ODA-FPA-0

shows two T_g s. We think this rationalize in terms of its untransparence which caused complex phase behavior. As the BPA-based polymers were concerned on, ODA-BPA-20 shows a T_g s at 204 $^{\circ}$ C, ODA-BPA-40 at 198 $^{\circ}$ C, and ODA-BPA-60 at 203 $^{\circ}$ C. Because the T_g s of BPA-based PEI and PES are similar (PEI at 216 $^{\circ}$ C and PES at 220 $^{\circ}$ C), the T_g s of their copolymers changed little when the content of dichlorophenylsulfone differed. The original storage modulus of the BPA-based polymers ranged from 1.62 to 1.98 GPa.. All of the polymers show amorphous patterns. It was well known that poly(ether sulfone) have a strong tendency to crystallize, which decreased the mechanical properties and the ability of film-forming. However, by copolymerization with bis(chlorophthalimide), the crystallinity was depressed successfully.

Table 1. Thermal and mechanical properties of polymers.

Polymer	$T_g(^{\circ}\text{C})^a$	$T_{5\%}(^{\circ}\text{C})^b$	Tensile strength(MPa)	Modulus (MPa)	Elongation (%)
ODA-FPA-0	204	482	112	2080	7.5
ODA-FPA-20	253	481	124	2100	8.9
ODA-FPA-40	256	507	110	2040	6.9
ODA-FPA-60	268	429	65	1900	3.5
ODA-BPA-0	- ^c	495	- ^c	- ^c	- ^c
ODA-BPA-20	204	493	117	2200	7.5
ODA-BPA-40	198	476	100	2090	5.2
ODA-BPA-60	203	437	72	1340	6.0

^a Obtained from DMTA at heating rate of 3 $^{\circ}$ C /min at 1 Hz.

^b Five percent weight loss obtained from TGA at a heating rate of 10 $^{\circ}$ C /min in air

^c Not measured because the film is brittle.

Conclusion A series of high-molecule-weight polyetherimides and their copolymers have been synthesized in one pot from bis(chlorophthalimide), dichlorodiphenylsulfone and bisphenolate using diphenylsulfone as the solvent. All of polymers show good solubility in common organic solvents. The 5% weight-loss temperatures of isomeric polyimides were 429-507 $^{\circ}$ C in air. The glass-transition temperatures (T_g s) of 4, 4'-(9-fluorenylidene) diphenol-based polymers increase as the ratios of diphenylsulfone increase, while the T_g s of biphenol A-based unconspicuously change when the ratios of diphenylsulfone increase. Either 4, 4'-(9-fluorenylidene) diphenol or biphenol A is used, the mechanical properties of copolymers are the best when the ratio of diphenylsulfone is 20%. The wide-angle X-ray diffraction showed that all polymers are amorphous. The crystalline tendency of polyethersulfone is depressed by copolymerization with polyetherimide.

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