

Preparation and Characterization of Fluorine-Containing Aromatic Polyacetals with Low Dielectric Constant and High Solubility

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Abstract

A series of fluorine-containing aromatic homopolyacetals and copolyacetals with a wide range of unit ratios were synthesized by the solution polycondensation of 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane (bisphenol AF), 2,2-bis(4-hydroxyphenyl)propane (bisphenol A), or both with 2-(trifluoromethyl)benzal chloride, and the effect of fluorine substitution on the properties of these polymers is discussed in relation to the fluorine contents.

Introduction

Attention has been focused on the preparation of fluorine-containing condensation polymers because of their unique properties and high performance.¹ A series of studies on the synthesis, characterization, and evaluation of fluorine-containing aromatic condensation polymers has revealed that hexafluoroisopropylidene-group-containing polymers, such as polyketones,² polyazomethines,³ polybenzimidazoles,⁴ polybenzothiazole,⁵ and/or their respective copolymers, have unique properties such as good solubility in organic solvents, toughness and flexibility at low temperatures, water and oil repellency, high thermal stability, and flame resistance in addition to the prominent characteristics inherent in the corresponding polymers without fluorine. Thus, the incorporation of hexafluoroisopropylidene groups into existing aromatic condensation polymers can not only make them soluble or processable but also give them additional characteristics.

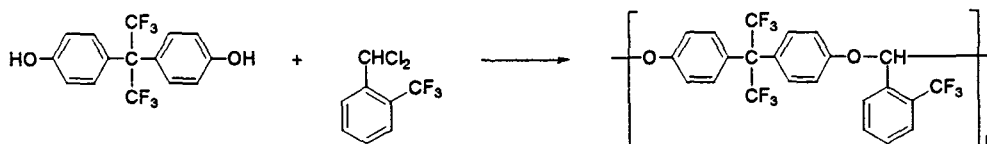
Because of the outstanding properties of thermal stability, transparency, impact resistance, and self-extinguishment, aromatic polycarbonates, such as that derived from bisphenol A, are ranked as high-performance engineering plastics. Structurally related aromatic polyformal has been obtained from bisphenol A and dichloromethane.⁶ This polymer also has prominent physical properties comparable to those of bisphenol A-based polycarbonate.⁷ We have already reported on the preparation and characterization of a series of hexafluoroisopropylidene-group-containing polycarbonates⁸ and polyformals⁹ derived from bisphenol AF, bisphenol A, or both. The physical properties of bisphenol A-based polycarbonate and polyformal, such as their solubility, mechanical, surface, and optical properties, and thermal stability, were successfully improved by fluorine substitution.

In this study, a series of fluorine-containing aromatic homopolyacetals and copolyacetals with a wide range of unit ratios were synthesized by the solution polycondensation of bisphenol AF, bisphenol A, or both with 2-(trifluoromethyl)benzal chloride, and the effect of fluorine substitution on the properties of these polymers is

discussed in relation to the fluorine contents.

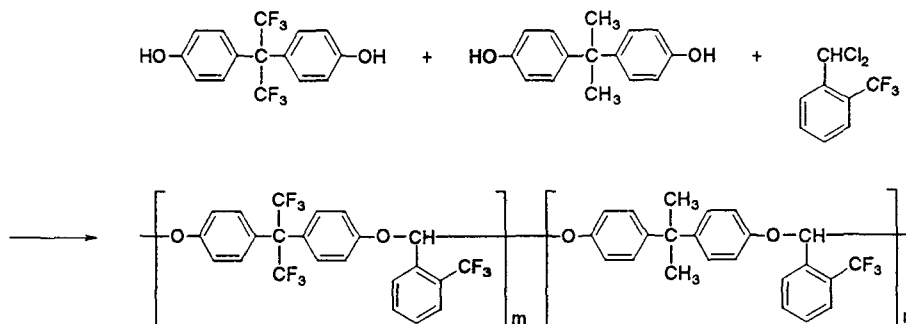
Results and Discussion

Bisphenol AF-based homopolyacetal was synthesized by the solution polycondensation of bisphenol AF with 2-(trifluoromethyl)benzal chloride in highly polar media in the presence of potassium hydroxide and 18-crown 6-ether at 100°C. Polar aprotic solvents such as DMAc, DMF, DMSO, HMPA, and NMP were used as media:



The optimum reaction conditions for the polycondensation of bisphenol AF with dichloromethane were reported previously,⁹ where the use of excess dichloromethane to bisphenol AF was required for producing polyformal of a high molecular weight. Thus, in this reaction the stoichiometry of bisphenol AF and dichloromethane does not have to be controlled because the first intermediate formed in the reaction, $-OCH_2Cl$, is more reactive than dichloromethane. Therefore, the effect of the amount of 2-(trifluoromethyl)benzal chloride on the reduced viscosity of the resulting polymer was first studied in NMP for 3 h. The viscosity value markedly increased with the increasing ratio of 2-(trifluoromethyl)benzal chloride to bisphenol AF. Thus, the use of excess 2-(trifluoromethyl)benzal chloride is also essential for the formation of the polyacetal with a high molecular weight. The media also had a remarkable effect both on the yield and reduced viscosity of the polymer obtained. The use of DMAc, DMSO, and NMP led to the formation of polyacetals with reduced viscosities higher than 0.5 dL/g in high yields. The polymerization in NMP proceeded relatively rapidly and was essentially completed in 3 h. The optimum reaction conditions thus obtained were 10 mmol of 2-(trifluoromethyl)benzal chloride, 20 mmol of potassium hydroxide, 0.75 mmol of 18-crown 6-ether, and 5 mL of NMP, on a 7.5 mmol scale of bisphenol AF, leading to the formation of bisphenol AF-based homopolyacetal having reduced viscosity of 0.58 dL/g in 86% yield at 100°C for 3 h.

A series of copolyacetals and bisphenol A-based homopolyacetal were synthesized by the reaction of bisphenol AF/bisphenol A mixtures at feed ratios of 80/20, 60/40, 50/50, 40/60, 20/80, and 0/100 with 2-(trifluoromethyl)benzal chloride under the aforementioned preferable conditions:



A series of copolyacetals were obtained quite readily with high reduced viscosities ranging from 0.43 to 0.97 dL/g and in high yields, regardless of the ratio of bisphenol AF (Table I).

Table I. Preparation and Thermal Properties of Bisphenol AF-Based and/or Bisphenol A-Based Homopolyacetals and Copolyacetals^a

Feed Ratio of Bisphenol AF/ Bisphenol A	Yield ^b %	η_{red} ^c dL/g	T_g ^d °C	DT ₅ ^e °C	DT ₁₀ ^f °C	RW ^g %
100: 0	86	0.58	131	346	352	58
80: 20	87	0.63	131	345	353	57
60: 50	88	0.50	127	333	342	57
50: 50	88	0.43	131	328	334	58
40: 60	89	0.87	131	322	330	60
20: 80	88	0.97	127	320	329	60
0:100	91	0.71	127	302	316	66

^a Polymerization was carried out with the bisphenols (7.5 mmol) and 2-(trifluoromethyl)benzal chloride (10 mmol) in NMP (5 mL) in the presence of potassium hydroxide (20 mmol) and 18-crown 6-ether (0.75 mmol) at 100°C for 3 h.

^b The yield was calculated on the basis of the theoretical structure.

^c Measured at a polymer concentration of 0.5 g/dL in NMP at 30°C.

^d Glass-transition temperature determined by DSC at a scan rate of 10K/min under nitrogen.

^e Temperature at which a 5% weight loss was recorded by TG at a heating rate of 10K/min under nitrogen.

^f Temperature at which a 10% weight loss was recorded.

^g Residual weight at 500°C under nitrogen.

Regardless of the fluorine content, these polymers all dissolved in highly polar solvents such as DMAc, DMF, HMPA, and NMP. They were also highly soluble in common organic solvents such as benzene, toluene, dichloromethane, chloroform, ethyl acetate, and tetrahydrofuran. Both bisphenol AF-based and bisphenol A-based homopolyacetals, two representative polyacetals, equally dissolved in toluene, ethyl acetate, and tetrahydrofuran up to a high concentration of 500 g/L at room temperature. The fluorine substitution generally enhances markedly the solubility of aromatic condensation polymers because the fluorine atom has a low intermolecular cohesive energy. Their high solubility behavior should be ascribed to the decrease of the energy and also to the reduction in both polymer chain packing and regularity due to the presence of 2-(trifluoromethyl)phenyl groups in the side chain. All the polyacetals gave colorless, transparent, and tough films when cast from the chloroform solutions and also when hot-pressed at temperatures greater than the respective T_g 's.

The tensile strength, elongation at break, and tensile moduli of the chloroform-cast films were 35 MPa, 2%, and 2.2 GPa for the bisphenol AF-based homopolyacetal; 39 MPa, 2%, and 2.4 GPa for the 50/50 bisphenol AF/bisphenol A-based copolyacetal; and 31 MPa, 2%, and 2.2 GPa for the bisphenol A-based homopolyacetal. This results indicates that the incorporation of hexafluoroisopropylidene groups into bisphenol A-type polyacetal has little effect on the mechanical properties of the films.

The thermal behavior data of the polyacetals are tabulated in Table I. The T_g 's of the polyacetals evaluated by DSC were around 130°C regardless of the fluorine contents. T_g 's have been reported by us to be 88-123°C for the polyformals derived

from dichloromethane,⁹ values that are lower than those of the polyacetals obtained here. The presence of bulky pendant 2-(trifluoromethyl)phenyl groups in these polymers increases the chain rigidity along the polymer backbone, consequently increasing the T_g 's. The TG curves of the polyacetals exhibited a 5% weight loss (DT5) at 302-346°C, a 10% weight loss (DT10) at 316-353°C, and residual weight at 500°C (RW) of 57-66% under nitrogen. Thus, the DT5 and DT10 tended to increase significantly and monotonously with increasing fluorine content. Because the methyl group is more susceptible to thermal degradation than aromatic rings, this behavior can be explained by a comparison of the thermal stability of the hexafluoroisopropylidene and isopropylidene groups.

The dielectric constant (ϵ') at 1 MHz were 2.43 for the bisphenol AF-based homopolyacetal and 2.68 for the bisphenol A-based homopolyacetal, both of which were remarkably lower than the value of the reference bisphenol AF-based homopolyformal,⁹ 2.88. It is, therefore, concluded from this result that the incorporation of 2-(trifluoromethyl)phenyl groups into the side chain is more effective than the incorporation of hexafluoroisopropylidene groups into the polymer backbone for the depression of ϵ' .

Conclusions

A series of fluorine-containing aromatic homopolyacetals and copolyacetals with a wide range of unit ratios were easily synthesized through the solution polycondensation of bisphenol AF, bisphenol A, or both with 2-(trifluoromethyl)benzal chloride. The incorporation of hexafluoroisopropylidene groups into the bisphenol A-type polyacetals successfully brought about an increase in the thermal stability and an decrease in the dielectric constant of the polymers, whereas the film properties were scarcely affected by the modification. The soluble polyacetals obtained are thought to be promising electric insulation materials for fields in microelectronics.

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