

Preparation and Properties of Hexafluoroisopropylidene-Group-Containing Aromatic Condensation Polymers

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Abstract

Three types of hexafluoroisopropylidene-group-containing aromatic condensation polymers, polycarbonate, polyformal, and polyacetal, and the respective copolymers with a wide range of unit ratios were synthesized by the two-phase phase-transfer catalyzed or solution polycondensation of 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane, 2,2-bis(4-hydroxyphenyl)propane (bisphenol A), or both with trichloromethyl chloroformate, dichloromethane, and 2-(trifluoromethyl)benzal chloride, respectively, and the effect of the fluorine substitution on the preparation and properties of these polymers was discussed with relation to the fluorine contents. The incorporation of fluorine atom into bisphenol A-type of polycarbonate, polyformal, and polyacetal successfully improved the physical properties of the resulting polymers, such as solubility, mechanical, surface, optical, and dielectric properties, and thermal behavior.

Introduction

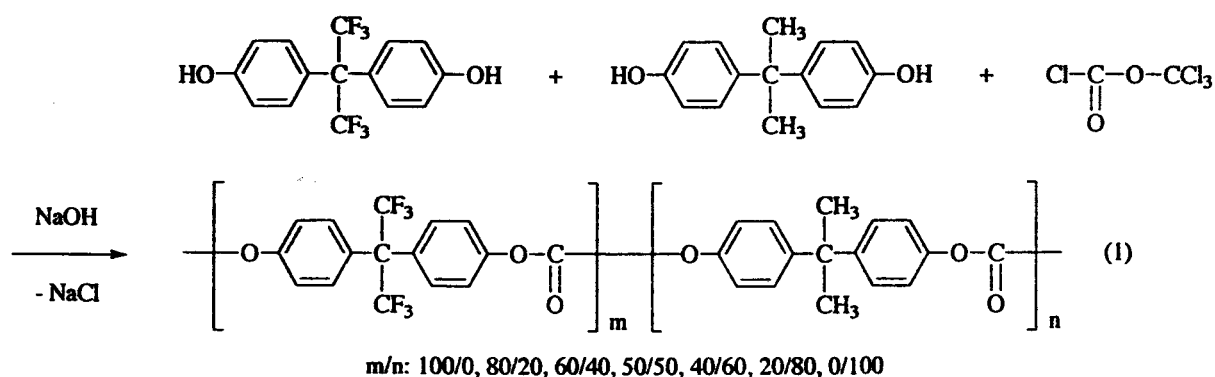
Attention has been focused on the preparation of fluorine-containing condensation polymers because of their unique properties and high performance.¹ A series of our studies on the synthesis, characterization, and evaluation of fluorine-containing aromatic condensation polymers has revealed that hexafluoroisopropylidene (HFIP)-group-containing polymers, such as polyketones,² polyazomethines,³ polybenzimidazoles,⁴ polybenzothiazoles,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 HFIP groups into existing aromatic condensation polymers can not only make them soluble or processable but also give them additional characteristics. All these outstanding properties are attributed solely to the fluorine substituent, which has peculiar properties such as high electronegativity, low intermolecular

cohesive energy, lower electronic polarizability, and high C-F bond energy.

In this paper, as a part of our series studies, I would like to introduce the synthesis and properties of three types of HFIP-group-containing aromatic condensation polymers, polycarbonates, polyformals, and polyacetals, derived from 2,2-bis(4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane (bisphenol AF).

HFIP-Group-Containing Polycarbonates⁶

A series of HFIP-group-containing homopolycarbonate and copolycarbonates and bisphenol A-based homopolycarbonate were synthesized by reacting the respective mixtures of bisphenol AF/2,2-bis(4-hydroxyphenyl)propane (bisphenol A) feed ratios of 100/0, 80/20, 60/40, 50/50, 40/60, 20/80, and 0/100 with trichloromethyl chloroformate (TCF) (Scheme 1).



Moderate- to high-molecular-weight polycarbonates with reduced viscosities up to 0.73 dL/g were obtained through two-phase phase-transfer-catalyzed polycondensation in 1,2-dichloroethane (DCE)/aqueous sodium hydroxide with tetra-*n*-butylammonium bromide (TBAB) (Table 1). The viscosity values, however, decreased markedly with increasing feed ratio of bisphenol AF to bisphenol A. This is due to the lower nucleophilicity of bisphenol AF induced by strongly electron-withdrawing trifluoromethyl groups than that of bisphenol A.

All the fluorine-containing polycarbonates were soluble in various organic media such as chlorinated hydrocarbons, acetone, benzene, *m*-cresol, cyclohexanone, dioxane, ethyl acetate, pyridine, tetrahydrofuran (THF), and polar aprotic solvents, while bisphenol A-based homopolycarbonate was insoluble in tetrachloromethane, acetone, and ethyl acetate even on heating. The tensile strength, elongation at break, and tensile moduli of three typical polycarbonate films were 45 MPa, 3%, and 2.0 GPa for bisphenol A-based homopolycarbonate, 41 MPa, >60%, 1.5 GPa for bisphenol AF/bisphenol A (50/50)-based copolycarbonate, and 27 MPa, >60%, and 0.8 GPa for bisphenol AF-based homopolycarbonate. This result indicates that the introduction of fluorine atom into bisphenol

Table 1 Preparation and Surface and Thermal Properties of Bisphenol AF- and/or Bisphenol A-Based Homopolycarbonates and Copolycarbonates^a

| | Feed ratio: bisphenol AF/ bisphenol A | Unit ratio ^b : bisphenol AF/ bisphenol A | Yield ^c % | η_{red}^d dL/g | θ_w^e ° | T_g^f °C | T_g^g °C | DT ₁₀ ^h °C | RW ⁱ % |
|-----|---|---|-------------------------|------------------------|-------------------|---------------|---------------|-------------------------------------|----------------------|
| F ⊕ | 100/0 | 100/0 | 84 | 0.35 | 91 | 169 | 169 | 460 | 57 |
| ↑ | 80/20 | 81/19 | 79 | 0.19 | 91 | 163 | 160 | 442 | 48 |
| | 60/40 | 54/46 | 81 | 0.27 | 92 | 160 | 157 | 437 | 50 |
| | 50/50 | 47/53 | 80 | 0.28 | 91 | 158 | 156 | 436 | 48 |
| | 40/60 | 41/59 | 85 | 0.51 | 91 | 156 | 153 | 439 | 41 |
| | 20/80 | 19/81 | 75 | 0.54 | 90 | 152 | 148 | 434 | 45 |
| F ⊖ | 0/100 | 0/100 | 85 | 0.73 | 84 | 149 | 148 | 429 | 37 |

^a Polymerization was carried out with the bisphenols (5.00 mmol) and TCF (7.50 mmol) in DCE (37.5 mL) and water (30 mL) in the presence of TBAB (3.15 mmol) and sodium hydroxide (28.5 mmol) at room temperature for 1 h.

^b The unit ratio of bisphenol AF/bisphenol A in the copolymers was estimated by elemental analysis.

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

^d Reduced viscosity was measured at a polymer concentration of 0.5 g/dL in DMF at 30°C.

^e Contact angle by water was measured at 25°C in air.

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

^g Determined by TMA at a scan rate of 10K/min under nitrogen.

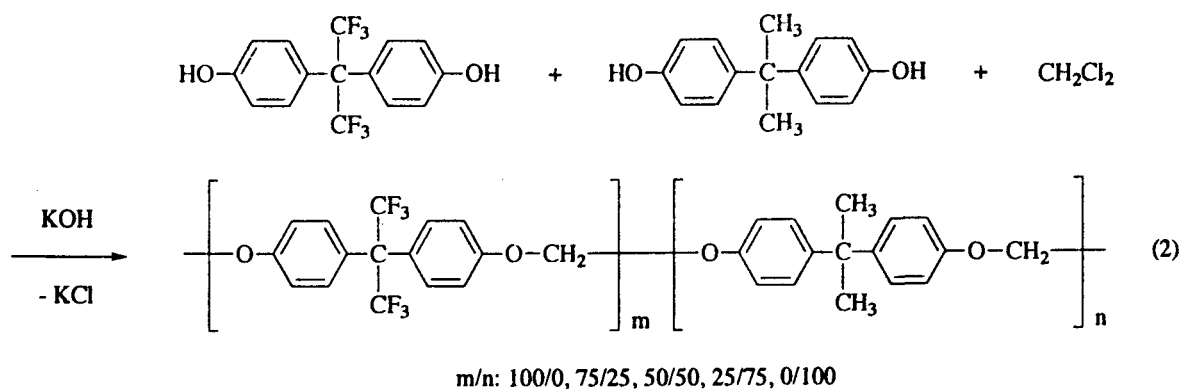
^h A 10% weight-loss temperature observed by TG at a heating rate of 10K/min in air.

ⁱ Residual weight at 500°C.

A-type of polycarbonate increases the pliability of films. The contact angles (θ_w) by water of the fluorine-containing polycarbonates were over 90°, regardless of their fluorine contents, whereas that of bisphenol A-based homopolycarbonate was 84° (Table 1). The critical surface tension and refractive index of bisphenol AF-based homopolycarbonate were respectively 20 dyn/cm and 1.426, both of which are significantly lower than well-known 45 dyn/cm and 1.585 of bisphenol A-based homopolycarbonate. The glass transition temperature (T_g) of bisphenol AF-based homopolycarbonate was 169°C, which is higher than that of bisphenol A-based homopolycarbonate by 20K. The T_g s of the copolymers increased monotonously between those of the two homopolymers as the bisphenol AF component was increased (Table 1). The TG curves of the polymers exhibited a 10% weight loss (DT₁₀) at 429-460°C and residual weight at 500°C (RW) of 37-57%, respectively, in air (Table 1). Thus, thermal stability of the polymers was clearly improved by introducing fluorine atom and increased monotonically with the increase in fluorine content.

HFIP-Group-Containing Polyformals⁷

A series of HFIP group-containing homopolyformal and copolyformals and bisphenol A-based homopolyformal were synthesized by the reaction of bisphenol AF/bisphenol A mixtures at feed ratios of 100/0, 75/25, 50/50, 25/75, and 0/100 with dichloromethane (DCM) (Scheme 2). In contrast to the polycarbonate syntheses, irrespective of the feed ratio of bisphenol AF,



high-molecular-weight polyformals with reduced viscosities of 1.4–5.3 dL/g were obtained through solution polycondensation in *N*-methyl-2-pyrrolidinone (NMP) in the presence of potassium hydroxide (Table 2).

Table 2 Preparation and Surface and Thermal Properties of Bisphenol AF- and/or Bisphenol A-Based Homopolyformals and Copolyformals^a

| Feed ratio: bisphenol AF/ bisphenol A | Unit ratio ^b : bisphenol AF/ bisphenol A | Yield ^c % | $\eta_{\text{red}}^{\text{d}}$ dL/g | $\theta_{\text{w}}^{\text{e}}$ ° | T_{g}^{f} °C | DT ₁₀ ^g °C | RW ^h % |
|---|---|-------------------------|--|-------------------------------------|---------------------------------|-------------------------------------|----------------------|
| 100/0 | 100/0 | 87 | 4.62 | 92 | 123 | 398 | 73 |
| 75/25 | 75/25 | 90 | 1.44 | 90 | 114 | 389 | 60 |
| 50/50 | 52/48 | 88 | 2.05 | 92 | 108 | 375 | 60 |
| 25/75 | 28/72 | 91 | 5.31 | 93 | 100 | 359 | 56 |
| 0/100 | 0/100 | 92 | 3.54 | 86 | 88 (88) ⁱ | 363 | 48 |

^a Polymerization was carried out with the bisphenols (5.00 mmol) and DCM (48 mmol) in NMP (5 mL) in the presence of potassium hydroxide (14 mmol) at 75°C for 4 h.

^b The unit ratio of bisphenol AF/bisphenol A in the copolymers was estimated by elemental analysis.

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

^d Reduced viscosity was measured at a polymer concentration of 0.5 g/dL in NMP at 30°C.

^e Contact angle by water was measured at 25°C in air.

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

^g A 10% weight-loss temperature observed by TG at a heating rate of 10K/min in air.

^h Residual weight at 500°C.

ⁱ Determined by TMA at a scan rate of 10K/min under nitrogen.

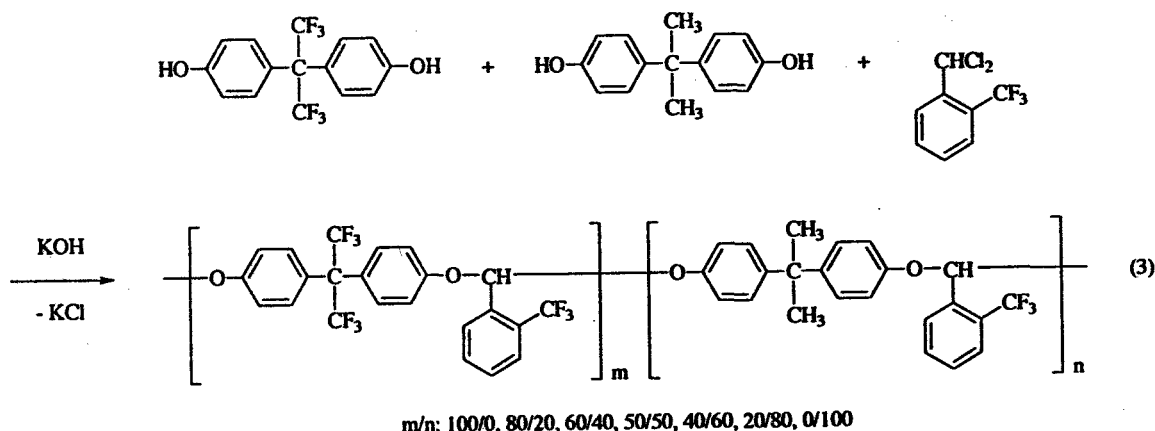
The difference in nucleophilicity between bisphenol AF and bisphenol A toward DCM is, however, considered to have a marked influence on the sequence distribution of comonomer units in the copolyformal chain. In these reactions, the use of excess DCM to bisphenols is required for producing the polyformals of high molecular weights. Thus, the stoichiometry of bisphenol and DCM does not have to be controlled because the first intermediate formed in the reaction, -OCH₂Cl, is more reactive than DCM. Thus, DCM acts as both reactant and solvent.

All the fluorine-containing polyformals were soluble in various organic solvents such as

chlorinated hydrocarbons, acetone, benzene, *m*-cresol, ethyl acetate, THF, toluene, and polar aprotic media. However, bisphenol A-based homopolyformal showed poorer solubility and dissolved only in DCM, chloroform, THF, hexamethylphosphoramide, and NMP. The tensile strength, elongation at break, and tensile moduli of three typical polyformal films were 38 MPa, 3%, and 1.5 GPa for bisphenol AF-based homopolyformal, 42 MPa, 4%, and 1.4 GPa for bisphenol AF/bisphenol A (50/50)-based copolyformal, and 44 MPa, 3%, and 2.1 GPa for bisphenol A-based homopolyformal. This result indicates that the introduction of fluorine atom into bisphenol A-type of polyformal has little effect on the mechanical properties of the films. The θ_w s by water of the fluorine-containing polyformals were over 90°, regardless of their fluorine contents, whereas that of bisphenol A-based homopolyformal was 86° (Table 2). T_g was 88°C for bisphenol A-based homopolyformal. The T_g s of bisphenol AF-based homopolyformal was 123°C, which is higher than that of bisphenol A-based homopolyformal by 35K. All the copolyformals showed single T_g s between those of the two homopolyformals, which increased monotonically with increasing bisphenol AF content (Table 2). The TG curves of the polymers exhibited a DT₁₀ at 359-398°C and RW of 48-73%, respectively, in air (Table 2). Thus, their thermal stability increased monotonically with the increase in bisphenol AF content.

HFIP-Group-Containing Polyacetals⁸

A series of HFIP-group-containing homopolyacetal and copolyacetals and bisphenol A-based homopolyacetal were synthesized by reacting the respective mixtures of bisphenol AF/bisphenol A feed ratios of 100/0, 80/20, 60/40, 50/50, 40/60, 20/80, and 0/100 with 2-(trifluoromethyl)benzal chloride (OTF) (Scheme 3).



Irrespective of the feed ratio of bisphenol AF, high-molecular-weight polyacetals with reduced viscosities of 0.43-0.97 dL/g were obtained through solution polycondensation in NMP in the presence of potassium hydroxide and 18-crown 6-ether (18-C-6) (Table 3). In these reactions,

Table 3 Preparation and Thermal Properties of Bisphenol AF- and/or Bisphenol A-Based Homopolyacetals and Copolyacetals^a

| Feed ratio: 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 |
| 60/40 | 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 |

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

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

^c Reduced viscosity was 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 A 5% weight-loss temperature observed by TG at a heating rate of 10K/min under nitrogen.

^f A 10% weight-loss temperature.

^g Residual weight at 500°C.

the use of excess OTF is also essential for the formation of the polyacetals with high molecular weights.

Regardless of the fluorine contents, these polymers all were highly soluble in various organic media such as chlorinated hydrocarbons, acetone, benzene, ethyl acetate, THF, toluene, and polar aprotic solvents. Both bisphenol AF-based and bisphenol A-based homopolyacetals, two representative polyacetals, equally dissolved in acetone, ethyl acetate, THF, and toluene up to a high concentration of 500 g/L. The tensile strength, elongation at break, and tensile moduli of three typical polyacetal films were 35 MPa, 2%, and 2.2 GPa for bisphenol AF-based homopolyacetal, 39 MPa, 2%, 2.4 GPa for bisphenol AF/bisphenol A (50/50)-based copolyacetal, and 31 MPa, 2%, and 2.2 GPa for bisphenol A-based homopolyacetal. This result also indicates that the introduction of fluorine atom into bisphenol A-type of polyacetal has little effect on the mechanical properties of the films. The T_g s of the polyacetals were around 130°C, regardless of the fluorine contents (Table 3). The TG curves of the polymers exhibited a 5% weight loss (DT₅) at 302-346, DT₁₀ at 316-353°C, and RW of 57-66%, respectively, under nitrogen (Table 3). Thus, both DT₅ and DT₁₀ increased significantly and monotonously with increasing fluorine content, whereas the T_g s were scarcely affected by fluorine substitution. The dielectric constant (ϵ') values at 1 MHz were 2.43 for bisphenol AF-based homopolyacetal and 2.68 for bisphenol A-based homopolyacetal, both of which were remarkably lower than the value of the reference bisphenol AF-based homopolyformal, 2.88 (Table 4). It is, therefore, concluded from this result that the

Table 4 Dielectric Constant of Bisphenol AF- and Bisphenol A-Based Homopolyacetals and the Reference Bisphenol AF-Based Homopolyformal

| Polymer | ϵ'^a |
|---------|---------------|
| | 2.88 |
| | 2.43 |
| | 2.68 |

^a Dielectric constant at 1 MHz measured by a bridge method at 22°C.

incorporation of trifluoromethyl groups into the side chain is more effective than the incorporation of HFIP groups into polymer backbone for the depression of ϵ' .

Conclusion

Three types of hexafluoroisopropylidene-group-containing aromatic condensation polymers, polycarbonates, polyformals, and polyacetals, and the respective copolymers with a wide range of unit ratios could be synthesized through the two-phase phase-transfer catalyzed or solution polycondensation by simple mixing of bisphenol AF and/or bisphenol A and trichloromethyl chloroformate, dichloromethane, and 2-(trifluoromethyl)benzal chloride, respectively. The incorporation of hexafluoroisopropylidene groups into bisphenol A-type of polycarbonate, polyformal, and polyacetal successfully brought about the increases in the solubility and thermal stability and the decreases in the wettability, refractive index, and dielectric constant of the polymers, whereas the film properties were scarcely affected by the modification. These soluble polymers are thought to be promising electric insulation materials for fields in microelectronics.

References

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