# Fluorinated Copolyimides Prepared by One-Shot and Stepwise Monomer Addition Method

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## SYNOPSIS

Copolyimides containing a hexafluoropropylidene group are prepared by the stepwise monomer addition method as well as the conventional one-shot method. The stepwise addition method goes through an oligomeric imide prepolymer. The molecular weight distribution of the prepolymers approximately follows the Flory's statistical distribution in the fluorinated imide prepolymer. Except for the final molecular weight, the conventional one-shot method does not give a significant difference in the copolymer character from the stepwise method, indicating that the segmental distribution in the copolyimides is practically statistical in the present monomer combination. The observed difference in the molecular weight by the preparation method may be related to the reactivity difference of the two monomer pairs. © 1995 John Wiley & Sons, Inc.
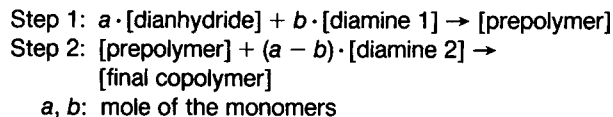
## INTRODUCTION

Polyimides are well known for their high temperature resistance and good mechanical properties.[1] In the past few years, fluorinated polyimides have drawn considerable interest because of their organic solubility, optical transparency, low dielectric constant, and high gas permeability.[1,2] Polyimides are generally synthesized by reacting stoichiometric amounts of a dianhydride and a diamine followed by dehydrating imide-ring formation. Copolymerization of polyimides is known to be an effective way to modify polymer characters[3–5] and is easily done by using more than two dianhydrides and diamines. Typically, copolycondensation is carried out by reacting dianhydride(s) and diamine(s) at the same time to form a copolyamic acid followed by the imidization. However, where the sequential segment distribution in the copolymer is concerned, the process may involve many complexities such as the reaction kinetics of the monomer pairs and interchange reactions of the segments.[6,7] Consequently, the composition and the sequential distribution of the segments may not be statistical or random as usually presumed.

We have applied the stepwise copolyimidization method[8] in which a diamine (or dianhydride) is reacted with excess amount of a dianhydride (or diamine) to form anhydride (or amine) terminated imide prepolymer (first step), and then a stoichiometric amount of the second diamine (or dianhydride) is added to obtain high polymer (second step). The reaction sequence is shown in Scheme 1.

With the stepwise process, there should be little chance of the interchange reaction between the segments because a complete imidization is accomplished at the first stage. Therefore, the sequential distribution of the two segments is expected to be consistent regardless of the reactivity of monomer pairs because each pair is not in the state of competitive reaction.

In the present article, characterization of fluorinated copolyimides prepared by the stepwise method as well as the conventional one-shot method are reported. In addition, the molecular weight distribution (MWD) of the prepolymers was examined. Application of the two-step method can provide a better characterization of the copolyimides without an uncertainty in its segmental distribution. The copolyimides are derived from hexafluoroisopropylidene-2,2-bis(phthalic acid anhydride) (6FDA), and two diamines, 2,2-bis[4-(4-aminophenoxy)phenyl]hexa-

Step 1: a · [dianhydride] + b · [diamine 1] → [prepolymer]
Step 2: [prepolymer] + (a − b) · [diamine 2] →
[final copolymer]
a, b: mole of the monomers

**Scheme 1** Stepwise synthesis of copolyimide.

fluoropropane (HFBAPP) and 9,9-bis(4-amino-phenyl)fluorene (FDA). The chemical structures of the monomers and the copolyimides are shown in Figure 1. The described fluorinated copolyimide has high optical transparency, organic solubility,[1] and gas permeability.[8]

## EXPERIMENTAL

### Chemicals

6FDA (E-Grade) was purchased from Hoechst Celanese Corp. (Short Hills, NJ). HFBAPP and FDA were purchased from Wakayama Seika Kogyo Co., Ltd. (Wakayama, Japan). All other chemicals were reagent grade and used without further purification.

### Polymer Synthesis

Phenolic solvents, m-cresol or a 7 : 3 mixture of phenol : 4-methoxyphenol, were used for the polymer synthesis. A prescribed amount of a dianhy-

dride and a diamine were placed in a four-necked separable flask fitted with a mechanical stirrer, a distillation trap with a condenser, and a dry nitrogen inlet. The solvent and a catalytic amount of pyridine were added to the flask. A solid content was set to about 25 wt %. About 10 vol % of toluene was also added as an azeotropic agent. A slow nitrogen flow through the flask was continuously employed throughout the reaction. The reaction solution was stirred at room temperature for 30 min and then at 180°C for 2 h (first step). The water of amic acid dehydration was removed from a distillation trap with toluene. After being cooled down, a prescribed amount of the second diamine dissolved in the solvents with toluene was added to the flask. The reaction solution was stirred at room temperature for 30 min and then at 180°C for 5 h (second step). The solution was poured into excess methanol and homogenized with a laboratory mixer. A precipitate was filtered and soaked in excess methanol overnight. The precipitate was again filtered and air dried. The obtained powder was finally dried in an oven at 160°C under reduced pressure for 8 h. The conventional one-shot preparation of the copolyimides was done at 180°C for 5 h. All other conditions were similar to the stepwise method described above. The homopolyimide from 6FDA and HFBAPP cannot be obtained with the thermal imidization process because of gelation. Therefore, it was prepared by the conventional chemical imidization method described elsewhere.[9]
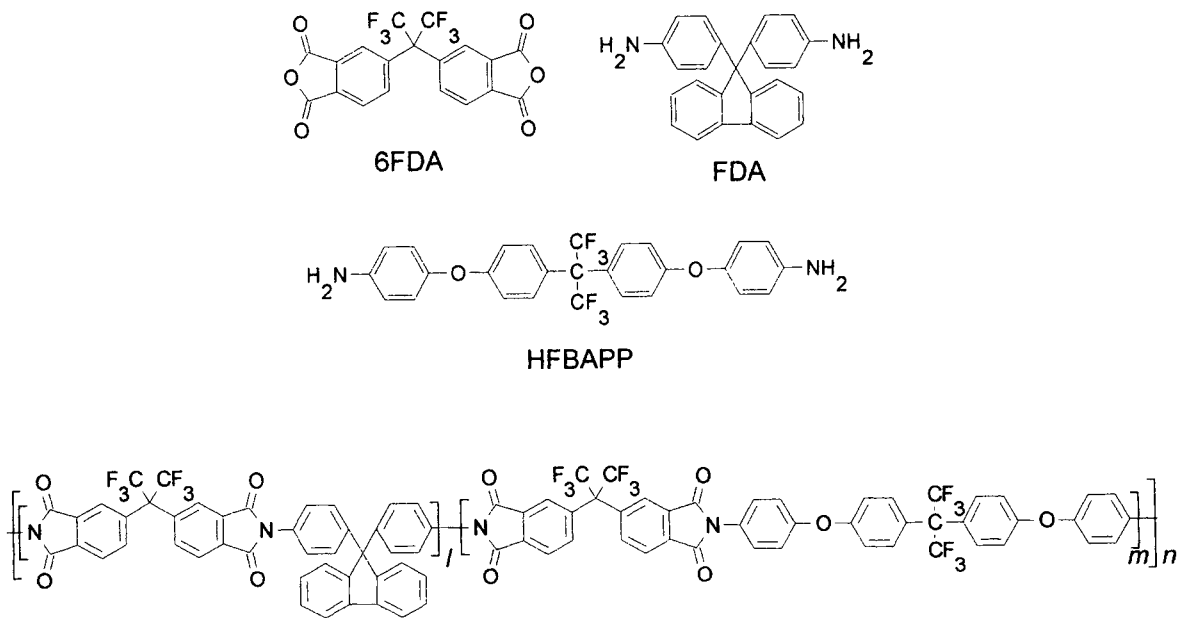


**Figure 1** Chemical structure of the monomers and the copolyimide.
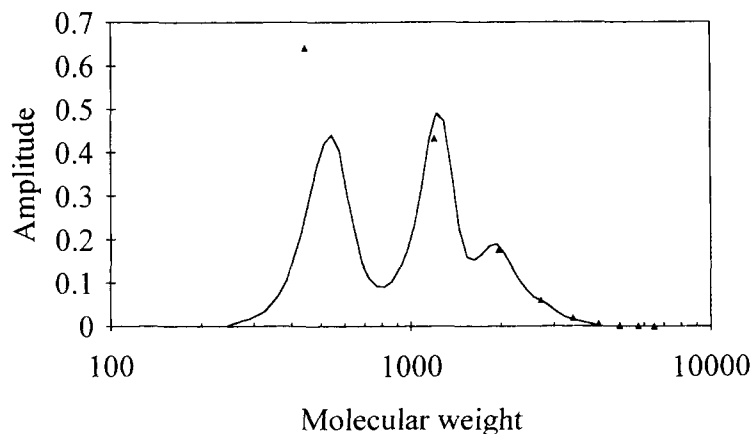
**Figure 2**   Molecular weight distribution of the oligomeric imide prepolymer, 6FDA/FDA (4 : 1). The solid line shows the observed distribution, and the filled triangle shows the calculated distribution according to the Flory's statistical treatment.

## Measurements

The differential scanning calorimetry (DSC) measurement was done with a Shimadzu DSC-50 apparatus with a heating rate of 10°C min$^{-1}$ up to 420°C under nitrogen atmosphere. The DSC was run twice consecutively, and the second run was used to determine the glass-transition temperature ($T_g$). The thermogravimetric analysis (TGA) was done using a Shimadzu TGA-50. The TGA was conducted with a heating rate of 10°C min$^{-1}$ up to 900°C under nitrogen atmosphere. FTIR measurement was done with a Nicolet FTIR spectrometer with the polymer films. The IR peak area was measured by the Nicolet software bundled with the spectrometer. Gel permeation chromatography (GPC) of the prepolymer was performed by a Hewlett–Packard Model 1090M HPLC system with 3 linear styrene-divinylbenzene GPC columns (5 $\mu$m, phenogel) running in THF at 40°C. A Tosoh TSKgel GMHXL column was also used for the copolyimides. The 6FDA/FDA prepolymer solutions (first step) were used directly for the GPC measurement. Complete imidization of the prepolymers were confirmed by imide carbonyl stretching peaks at 1785 and 1724 cm$^{-1}$ in the FTIR spectra; no amide carbonyl stretching peak was observed. Inherent viscosity of the polyimides were measured using a Östwald viscometer with a 0.5 g dL$^{-1}$ solution of N-methyl pyrrolidone (NMP) at 30°C. X-ray diffraction (XRD) was done with a Philips APD 3720 X-ray diffractometer. A d-spacing of a primary peak was calculated according to Bragg's condition, $\lambda = 2d \sin \theta$.

## RESULTS AND DISCUSSION

### MWD of Prepolymers

We first examined the stepwise reaction by GPC analysis of the imide prepolymers. The obtained MWD of the prepolymers is compared with the calculated distribution according to the Flory's statistical treatment.[6,10,11]

In the A-A plus B-B type step polycondensation (A reacts only with B and vice versa) with nonstoichiometric amount of the monomers, the number distribution of the oligomeric product species is derived according to the Flory's statistical treatment, under the usual assumptions of equal reactivity of the same functional groups and of the absence of intermolecular reactions. The product consists of three types of oligomers; terminated with A at one end and with B at the other (I), terminated with B at both ends (II), and terminated with A at both ends (III). The distribution function of the number of each product are expressed as follows:

(I)    $N_x(\text{I}) = 2 \cdot N_{AA} \cdot r^{x/2} \cdot p_A^{x-1}$

$$\times (1 - r \cdot p_A) \cdot (1 - p_A), \quad (1)$$

(II)    $N_x(\text{II}) = N_{AA} \cdot r^{(x-1)/2} \cdot p_A^{x-1} \cdot (1 - r \cdot p_A)^2, \quad (2)$

(III)    $N_x(\text{III}) = N_{AA} \cdot r^{(x-1)/2} \cdot p_A^{x-1} \cdot (1 - p_A)^2, \quad (3)$

where $x$ is the degree of polymerization ($x \geq 1$), $N_{AA}$ is the initial number of the A-A monomer, $r$ is the initial molar ratio of the A-A monomer ($N_{AA}$) vs. the B-B monomer ($N_{BB}$) ($r = N_{AA}/N_{BB} \leq 1$), and $p_A$ is the extent of the reaction of the A-A monomer
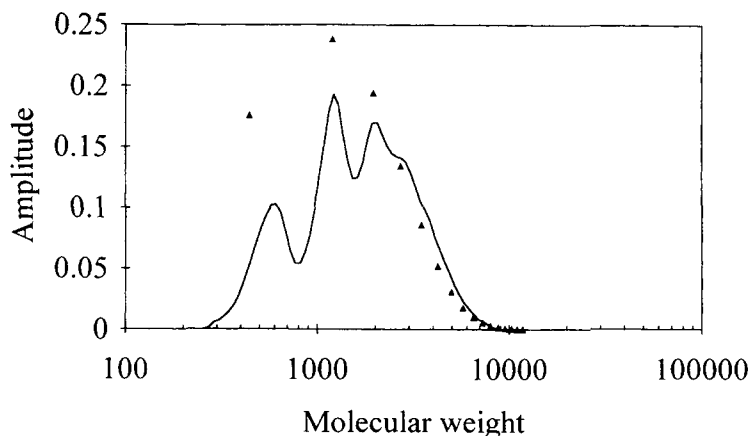
**Figure 3**   Molecular weight distribution of the oligomeric imide prepolymer, 6FDA/FDA (2 : 1). The solid line shows the observed distribution, and the filled triangle shows the calculated distribution according to the Flory's statistical treatment.

($p_B = rp_A$). If the reaction is complete ($p_A = 1$), $N_x(I)$ and $N_x(III)$ become zero, and only $N_x(II)$ (B group at both end) remains. The distribution function, $N_x$, [$=N_x(II)$] is then reduced to:

$$N_x = N_{AA} \cdot r^{(x-1)/2} \cdot (1 - r)^2. \qquad (4)$$

In the present study, a complete reaction at the first step was confirmed by FTIR measurement of the characteristic imide peaks. The GPC results can therefore be compared with eq. (4). The weight distribution function $W_x$ is simply calculated by the equation,



**Figure 4**   Relationship between the HFBAPP segment molar ratio and the FTIR absorption peak area ratio of 1176 and 1786 cm$^{-1}$.

$$W_x = w_x N_x / \Sigma w_x N_x, \qquad (5)$$

where $w_x$ is the molecular weight of the $x$-mer prepolymer, which can be calculated from the molecular weight of the monomers.

Figure 2 shows observed MWD of the 6FDA/FDA (4 : 1) prepolymer along with the calculated MWD according to eq. (5). The 6FDA/FDA (2 : 1) prepolymer is shown in Figure 3. For the present 6FDA/FDA oligoimides, the viscosity factor relative to polystyrene standard was found to be 1.3. The observed MWD shown in the figures are corrected with the factor. The calculated distributions fit reasonably well with the observed MWDs in both cases. It can be concluded that the MWD of the prepolymers approximately follows the classical statistical theory. It should be noted, however, that the amount of the remaining unreacted 6FDA appears less than the theoretical amount. This is probably due to the reactivity difference of the terminal groups in the monomer and in the oligomers.*
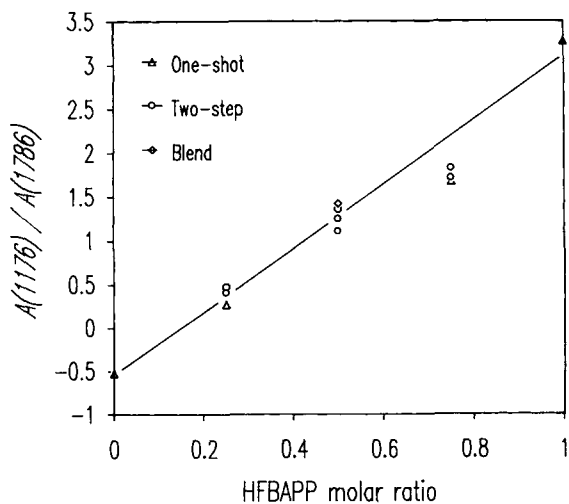
## Copolyimide Characterization

The HFBAPP segment ratio in the copolyimides were evaluated by FTIR absorbance peak area measurement with phenyl ether absorption peak at 1176 cm$^{-1}$ (integer between 1164 and 1185 cm$^{-1}$) and im-

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* Preliminary study of biphenyl tetracarboxylic dianhydride (BPDA) prepolymers showed larger deviation from the Flory's distribution than the 6FDA prepolymers. Reactivity difference of the first and the second anhydride group in BPDA is expected to be larger than in 6FDA due to their electron conjugation systems. It is therefore postulated that the deviation is attributed to the difference between a monomer and oligomers.
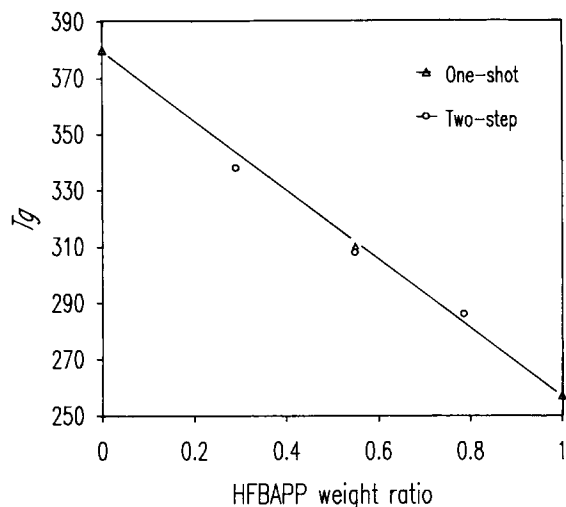
**Figure 5**  Relationship between the HFBAPP segment weight ratio and glass-transition temperature, $T_g$.

ide carbonyl symmetric stretching peak at 1786 cm$^{-1}$ (integer between 1767 and 1805 cm$^{-1}$). The absorption peak area ratio, A(1176)/A(1786), is plotted against the initial HFBAPP molar ratio in Figure 4. The area ratio of a blend film of the two homopolyimides is also shown in Figure 4. If all the HFBAPP is converted into the polymer, the points should be on a straight line intersecting at the origin in theory. Although the line does not meet the origin, a good linear correlation can be seen in Figure 4. It should be noted that the integral of the same peak region (1164–1185 cm$^{-1}$) in the 6FDA/FDA homopolyimide spectrum showed a negative value due to the existence of adjacent peaks. The peak area ratio calculated from the negative area is shown in Figure 4. The point is coincident with a zero extrapolation of the correlation line. This suggests that the observed shift of the correlation line is likely an artifact generated by the baseline determination of the 1176 cm$^{-1}$ peak. As seen in Figure 4, the observed ratios are not affected by the preparation processes. It is concluded that the segment content in the copolymers is consistent with the initial monomer ratio regardless of the monomer addition procedure.

Table I summarizes the characterization results of the copolyimides. Decomposition temperature does not vary among the copolyimides. Generally, the molecular weight of the copolyimides increases with increasing ratio of HFBAPP, as shown by the inherent viscosity and GPC results. According to XRD results, all the samples are basically non-crystalline, and no significant difference in the

amorphous $d$-spacing is seen between the preparation processes. Note that the HFBAPP homopolyimide shown in Table I was obtained with the chemical imidization method and therefore cannot be directly compared with the other copolymers.

Figure 5 depicts the relationship between HFBAPP segment weight ratio and $T_g$. The figure shows that the linear relationship between the segment weight ratio and $T_g$ regardless of the polymerization process. The $T_g$ of a copolymer frequently obeys the well-known Fox equation[12]:

$$1/T_g = w_1/T_{g_1} + w_2/T_{g_2}$$

where $w_1$ and $w_2$ are the weight fraction of component 1 and component 2, and $T_{g_1}$ and $T_{g_2}$ are the $T_g$ of the homopolymers of component 1 and component 2, respectively. The equation has a negative deviation from the simple linear correlation with the segment weight ratio. As mentioned in the previous article,[8] the linear relation of the copolyimides may be due to their weak interchain segmental interaction comparing to the strong intrachain segmental interaction. The situation is implemented by the hexafluoroisopropylidene group that considerably lowers the cohesive energy density, while increasing the chain rigidity by hindering the rotation about the group. Under the given condition, it is expected that the segmental sequence may influence $T_g$. No effect of the preparation process on $T_g$ suggests that there should
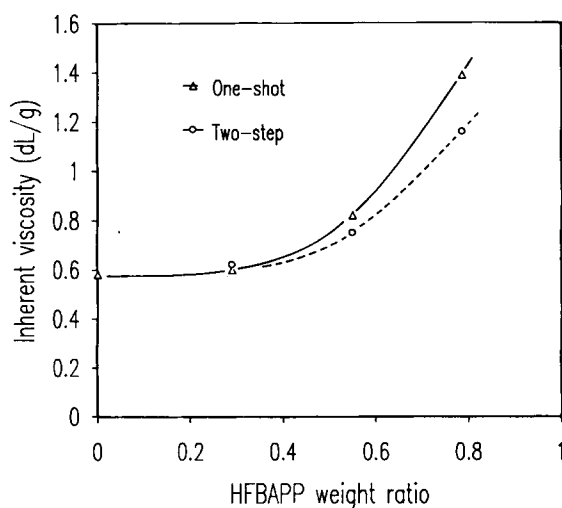


**Figure 6**  Relationship between the HFBAPP segment weight ratio and the inherent viscosity in NMP (0.5 g dL$^{-1}$).

**Table I    Characterization Results of 6FDA(A)/FDA(B)HFBAPP(C) Copolyimides**

| Sequence[a] | $\eta_{inh}$ (dL g$^{-1}$) | $T_g$[b] (°C) | $d$-Spacing (Å) | Decomp.[c] (°C) | $M_w$[d] | $M_w/M_n$ |
|---|---|---|---|---|---|---|
| (4)A + (4)B | 0.58 | 380 | — | 539 | 69000 | 2.4 |
| (4)A + (3)B + (1)C | 0.60 | 338 | 5.48 | 533 | 95400 | 1.7 |
| (4)A + (3)B → +(1)C | 0.62 | 338 | 5.45 | 531 | 109000 | 1.8 |
| (4)A + (1)C → +(3)B | 0.61 | 339 | 5.38 | 535 | 105000 | 1.7 |
| (4)A + (2)B + (2)C | 0.82 | 310 | 5.24 | 531 | 201000 | 2.5 |
| (4)A + (2)B → +(2)C | 0.75 | 308 | 5.21 | 535 | 115000 | 1.7 |
| (4)A + (1)B + (3)C | 1.39 | 286 | — | 543 | 419000 | 3.5 |
| (4)A + (1)B → +(3)C | 1.16 | 286 | 5.24 | 532 | 373000 | 2.7 |
| (4)A + (4)C | (0.53) | 257 | — | 521 | (99000) | (2.2) |

[a] A + B + C represents one-shot process, and A + B → +C and A + C → +B represent two-step process. Numbers in parentheses are the molar ratio of the monomers, A, B, and C.
[b] DSC method.
[c] TGA method. Onset temperature.
[d] Calibrated with polystyrene standard. No correction was made.

be little sequential difference due to the preparation process.

Figure 6 depicts the change in the inherent viscosity with the HFBAPP ratio. A clear correlation between the HFBAPP weight ratio and viscosity can be seen. The GPC result is consistent with the viscosity measurement as shown in Table I. The results show an increase in the molecular weight with increasing HFBAPP content. In addition, the sharp increase of the molecular weight is observed at higher HFBAPP ratio. Coupled with the gelation of 6FDA/HFBAPP homopolyimide upon thermal imidization, a part of the increase in the molecular weight may be attributed to a crosslinking of the HFBAPP segment.

There is a consistent tendency of the stepwise [A + B → +C] process in both GPC and the viscosity results. At higher HFBAPP ratio, the one-shot method gives higher molecular weight than the stepwise method. On the other hand, the stepwise process does not give a significant difference in the molecular weight from the one-shot process, or the stepwise method shows even higher molecular weight at lower HFBAPP ratio. The 6FDA/FDA pair is less reactive than the 6FDA/HFBAPP pair in terms of a molecular weight buildup. At higher HFBAPP ratio, the one-shot method allows HFBAPP to have more accessibility to moieties where it builds up the molecular weight including the crosslinking. At lower HFBAPP content, the stepwise method may offset the poor FDA reactivity by providing excess acid anhydride at the first stage. Overall, the stepwise method gives comparable molecular weight to the one-shot method at lower HFBAPP content.

## CONCLUSION

The two-step preparation method of copolyimides in which the copolymerization goes through the acid terminated oligomeric imide prepolymer was described. The GPC analysis of the oligomeric prepolymer shows that their MWD can be approximately described by the Flory's statistical method. Except for the molecular weight, the characterization results of the 6FDA copolyimides prepared by the conventional one-shot method do not have significant difference from those of the copolyimides by the two-step method. The results indicate that the segment composition and sequential distribution are practically identical in the copolyimide prepared by either method, and the distribution is approximately statistical. However, the preparation process appears to have an effect on the final molecular weight of the copolyimides. At a higher ratio of the reactive HFBAPP, the stepwise method with reacting FDA at first, yields lower final molecular weight than the conventional one-shot method. While at lower HFBAPP ratio, the stepwise method shows comparable or even higher molecular weight than the one-shot method. The observed difference is likely related to a difference in polymerization kinetics of the two monomer pairs, that affects the one-shot method heavily, but the stepwise method minimally.[†]

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[†] We have observed that high MW can be achieved only by the two-step method in some copolyimides, especially in the case of comonomer pairs having considerably different reactivity.

## REFERENCES

1. T. L. St. Clair, in *Polyimides,* D. Wilson, H. D. Stenzenberger, and P. M. Hergenrother, Eds., Blakie and Son Ltd., Glasgow and London, 1990, Chap. 3, p. 58.

2. A. K. St. Clair, T. L. St. Clair, and W. S. Slemp, in *Recent Advances in Polyimides: Synthesis, Characterization and Applications,* W. Weber and M. Gupta, Eds., Plenum Press, New York, 1987, p. 16.

3. E. Akiyama, Y. Takamura, and Y. Nagase, *Makromol. Chem.,* **193,** 1509 (1992).

4. G. Zoia, S. A. Stern, A. K. St. Clair, and J. R. Pratt, *J. Polym. Sci., Polym. Phys. Ed.,* **32,** 53 (1994).

5. D. M. Stoakley, A. K. St. Clair, and ⌐. I. Croall, *J. Appl. Polym. Sci.,* **51,** 1479 (1994).

6. P. Manaresi and A. Munari, in *Comprehensive Polymer Science, Vol. 5, Step Polymerization,* G. C. Eastmond, A. Ledwith, S. Russo, and P. Sigmalt, Vol. Eds., Pergamon Press, Oxford, U.K., 1989, Chaps. 3 and 4, p. 35.

7. E. Maréchal and A. Fradet, in *Comprehensive Polymer Science, Vol. 5, Step Polymerization,* G. C. Eastmond, A. Ledwith, S. Russo, and P. Sigmalt, Vol. Eds., Pergamon Press, Oxford, U.K., 1989, Chap. 16, p. 251.

8. B.-W. Chun, C. Ishizu, H. Itatani, K. Haraya, and Y. Shindo, *J. Polym. Sci., Polym. Phys. Ed.,* **32,** 1009 (1994).

9. R. A. Hayes, U.S. Pat. 4,705,540 (Nov. 10, 1987); 4,717,393, (Jan. 5, 1988); and 4,717,394 (Jan. 5, 1988).

10. P. J. Flory, *J. Am. Chem. Soc.,* **58,** 1877 (1936).

11. P. J. Flory, *Principles of Polymer Chemistry,* Cornell University Press, Ithaca, New York, 1953.

12. T. G. Fox, *Bull. Am. Phys. Soc.,* **1,** 123 (1956).