Free Radical Copolymerization of Furfuryl Acrylate and 2-Hydroxyethyl-Methacrylate

Dedicated to the memory of Professor Miguel Valero

DIONISIO ZALDÍVAR,[1] CARLOS PENICHE,[2] ANNA BULAY,[3] and JULIO SAN ROMÁN[4]*

[1]Laboratorio de Materiales Sintéticos (LMS), Universidad de La Habana, 10400 Havana, Cuba, [2]Facultad de Química, Universidad de La Habana, 10400, Havana, Cuba, [3]NPO "Plastmassi," 111 112 Moscow, Petrovskyi Proezd 35, Russia, [4]Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva 3, 28006–Madrid, Spain

SYNOPSIS

Copolymers of furfuryl acrylate (**F**) and 2-hydroxyethyl methacrylate (**H**) were prepared by free radical polymerization in DMF solution at 50°C, using 2,2'-azobisisobutyronitrile (AIBN) as initiator. The reactivity ratios of both monomers were calculated according to the general copolymerization equation using the Fineman–Ross and Kelen–Tüdös linearization methods, as well as the Tidwell and Mortimer nonlinear least-squares treatment. The reactivity ratios obtained were $r_F = 0.93$ and $r_H = 1.42$. The microstructure of copolymer chains is described on the basis of first-order Markov statistics, and the copolymer glass transition temperatures were determined calorimetrically. The variation of T_g with the copolymer composition is discussed according to modern methods, considering the sequence distribution of monomeric units along the copolymer chains. Also the T_g of the corresponding homopolymers was determined giving the values $T_g(F) = 321$ K and $T_g(H) = 358$ K, whereas the T_g of the corresponding alternating diad has an average value of $T_{gFH} = 326$ K. © 1993 John Wiley & Sons, Inc.

Keywords: copolymers • furfuryl acrylate • hydroxyethyl methacrylate • biomaterials • glass transition temperature

INTRODUCTION

The use of raw materials from renewable sources has claimed the attention of a great number of scientific research groups during the last three decades, and compounds derived from 2-furfuraldehyde were extensively used during the sixties and seventies because of its accesibility from vegetable residues such as corn husks and sugar cane.[1] Although a pioneer work by Fisher and Rehberg[2] reported the formation of crosslinked polymers when furfuryl esters of acrylic and methacrylic acids were polymerized by free radical initiator, Mihajlov and Boudevska[3] demonstrated that when furfuryl methacrylate or 5-carbomethoxyfurfuryl methacrylate were polymerized in bulk with free radical catalysts, insoluble crosslinked polymers were obtained, but the poly-

merization in solution provided soluble polymers.[4] Bevington and Harris[5] reported the formation of soluble copolymers when furfuryl methacrylate is copolymerized with methyl methacrylate in bulk (at low conversion) using AIBN as free radical initiator. Patel et al.[6,7] have successfully polymerized tetrahydrofurfuryl methacrylate for the preparation of dental filling materials and acrylic cements for orthopaedic surgery, and more recently[8] we have reported the preparation of soluble copolymers by the free radical copolymerization of furfuryl methacrylate with N-vinylpyrrolidone using AIBN as initiator.

However, it is well known that the hydrophilic or hydrophobic character of biomaterials can be controlled by preparing copolymer systems with a suitable composition and distribution of amphiphilic monomers along the copolymer chains. In this sense, 2-hydroxyethyl methacrylate has been widely used in the design and preparation of copolymer systems[9–13] because of the amphiphilic properties of

---

poly(2-hydroxyethyl methacrylate)[9,12] and its excellent biocompatibility.[9,10,14] In the present article, the free radical copolymerization of furfuryl acrylate with 2-hydroxyethyl methacrylate is described.

EXPERIMENTAL

Monomer Preparation and Purification of Materials

Furfuryl acrylate (F) was prepared by transesterification of methyl acrylate with furfuryl alcohol in the presence of sodium carbonate as catalyst and ionol as inhibitor. The product was distilled, dissolved in chloroform, and passed through a chromatographic column containing Silica Gel 60 (Macherey-Nagel, Germany). The eluent was analyzed by thin layer chromatography using Kieselgel 60 F 254 (Merck) as the stationary phase. The selected fraction was roto-evaporated in order to separate the solvent and distilled.

2-Hydroxyethyl methacrylate (H), supplied by Hydron Europe Ltd., containing less than 0.05 wt % of ethylene glycol dimethacrylate, was distilled under reduced pressure of nitrogen and the fraction of bp 87–89°C/5 mm Hg was collected.

2,2'Asobisisobutyronitrile (AIBN) was purified by fractional crystallization from methanol, mp 104°C.

N,N-dimethylformamide (DMF) was dried over anhydrous magnesium sulphate for 2 days and later with phosphoric anhydride overnight. After drying, DMF was distilled under reduced pressure of nitrogen. Other reagents were of extra-pure grade and used as purchased.

Copolymerization

Copolymerization reactions were performed in DMF solution at $50 \pm 0.1°C$, in pyrex glass ampoules sealed off under high vacuum. Monomer and initiator concentrations were 1.0 mol/L and 1.5×10^{-2} mol/L, respectively. The sealed ampoules were shaken vigorously and immersed in a water bath held at the required temperature of polymerization. After the proper reaction time, the ampoules were removed from the bath and at once the contents were poured into a large excess of diethyl ether. The precipitated samples were washed with the precipitant mixture and dried under vacuum until constant weight was attained.

Polymer Characterization

The copolymers obtained from different mixtures of F and H were analyzed by ^1H-NMR spectroscopy with a Bruker AM-200 spectrometer working at 200 MHz. The spectra were recorded at 40°C in 5% (w/v) deuterated dimethylsulphoxide solutions, with a 2400 Hz spectral width, flip angle of 30° ($2 \mu s$ pulse), a pulse repetition time of 2 s and 128 transients. A 16 K FID was acquired and zero filled to 32 K before Fourier transformation.

Differential Scanning Calorimetry (DSC)

Glass transition temperatures were determined with a Perkin-Elmer DSC-4 calorimeter. Measurements and calibration were carried out at a heating rate of 10°C/min. T_g was taken as the midpoint of the transition region. Samples (~ 40 mg weight) were introduced into the aluminium pan, heated at 450 K, compressed and then quenched at room temperature before performing the measurements. Measurements taken at heating rates of 5 and 15°C/min gave values of T_g with a deviation lower than 2% with respect to those obtained at 10°C/min.

RESULTS AND DISCUSSION

The copolymerization of furfuryl acrylate with 2-hydroxyethyl methacrylate in anhydrous DMF solutions was studied in a wide composition interval with molar fractions of F ranging from 0.15 to 0.85 in the monomer feed. The reaction time was initially regulated to reach conversions lower than 5 wt %, in order to satisfy the differential copolymerization equation.[15] The molar fraction of monomer units incorporated in the copolymer was determined from the ^1H-NMR spectra of copolymer samples prepared with different monomer feeds.

Figure 1 presents the spectra obtained for copolymers prepared with 30.0, 50.0, and 85.0 mol % of furfuryl acrylate in the feed. The analysis was performed by comparing the integrated intensities of resonance signals with chemical shifts of 6.45 and 6.55δ, assigned to the protons in position 3 and 4 of the aromatic furfuryl ring and 3.65 and 3.95δ, assigned to the oxyethylene protons of the $HO—CH_2—CH_2—$ side residue of 2-hydroxyethyl methacrylate units. The data of molar composition of the initial mixtures of comonomers used and of the resulting copolymers are quoted in Table I.

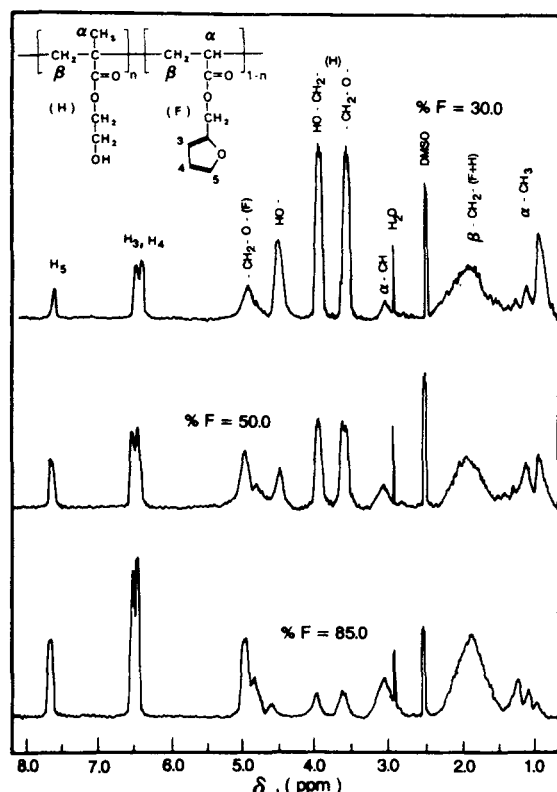The reactivity ratios of the monomers were de-

Figure 1. ^{1}H-NMR (200 MHz) spectra of **F–H** copolymers prepared with the molar composition of the monomers feed indicated in the figure.

termined according to the general copolymer composition equation by the application of the Tidwell and Mortimer nonlinear least-squares analysis.[16] To this end, initial approximated values of r_F and r_H were obtained by means of the Fineman–Ross[17] and Kelen-Tüdos[18] linearization methods. The results are shown in Table II. It must be pointed out that although the r_F and r_H values obtained using the linearization methods are somewhat different, they give the same reactivity ratios when feed to the nonlinear least squares method. We stress here that the reactivity ratios determined by the application of the analysis suggested by Tidwell and Mortimer[16] are the most probable values for this system. In this sense, the 95% confidence limit gives an idea of the experimental error and the correctness of the experimental conditions used to generate the composition data.[16] When the experimental error is reasonably small and the data have been taken under the appropriate conditions, the approximation can be remarkably good. This is illustrated by the dimensions of the elliptical diagram generated by the application of the mathematical treatment suggested

by Behnken[19] and Tidwell and Mortimer.[16] The application of this treatment to the copolymerization data reported in Table I and the reactivity ratios quoted in Table II provide the 95% confidence limits defined by the area of the elliptical diagram drawn in Figure 2. This diagram confirms the excellent approximation of the values of r_F and r_H as indicated by the reduced dimensions of the ellipse.

The average composition diagram shown in Figure 3 has been drawn with the Tidwell and Mortimer r_F and r_H values, using the Lewis–Mayo classical copolymerization equation; the experimental composition data fit adequately the theoretical diagram represented by the solid line. The reactivity of growing radicals with **F** ends, as measured by the ratio $1/r_F$ and the reactivity of the growing radical with **H** ends, as measured by the ratio $1/r_H$, are rather similar towards both monomers and the product $r_F r_H$ is close to unity, indicating that the system behaves almost ideally.

From the values of the reactivity ratios r_F and r_H given in Table II and taking into account well known statistical relationships, we have determined the "run number," R, defined by Harwood and Ritchey[22] as the average number of monomer alterations in a copolymer per 100 monomeric units. This parameter provides a useful picture of the sequence distribution in a copolymer chain and can be used to estimate the variation of the physical properties of copolymers with the composition. Values of R have been determined in terms of reactivity ratios and probability statistics for different values of the molar fraction of **F** in the feed, covering a wide interval of compositions. Figure 4 shows the variation of R with the molar fraction of **F** in the monomer feed. The maximum value of $R = 46.5$ is reached for a **F** molar fraction in the feed about 0.55.

Table I. Composition and Conditional Probabilities Data of the Free Radical Copolymerization of Furfuryl Acrylate (**F**) and 2-Hydroxyethyl Methacrylate (**H**), in DMF Solution at 50°C

Feed F_F[a]	Copolymer f_F[a]	Conversion (wt %)	P_{FH}	P_{HF}
0.150	0.12$_0$	2.3	0.859	0.111
0.300	0.24$_2$	2.7	0.714	0.232
0.500	0.44$_3$	3.2	0.517	0.413
0.700	0.68$_1$	2.4	0.315	0.622
0.850	0.82$_2$	3.4	0.159	0.800

[a] F_F and f_F are the molar fraction of furfuryl acrylate in the monomer feed and in the copolymer samples, respectively.

Table II. Copolymerization Parameters of the Free Radical Copolymerization of Furfuryl Acrylate with 2-Hydroxyethyl Methacrylate

Method	r_F	r_H	$r_F r_H$	$1/r_F$	$1/r_H$
Fineman–Ross	0.82 ± 0.4	1.25 ± 0.15	1.025	1.22	0.80
Kelen–Tüdos	0.88 ± 0.19	1.35 ± 0.08	1.188	1.14	0.74
Tidwell–Mortimer	0.93	1.42	1.321	1.07	0.71

The statistical distribution of **F** centered triads were determined considering the equations for the first-order Markovian transition probabilities P_{FH}, P_{HF}, P_{FF}, and P_{HH} according to the following equations[23]:

$$P_{FH} = 1 - P_{FF} = 1/(1 + r_F X) \quad (1)$$

$$P_{HF} = 1 - P_{HH} = 1/(1 + r_H/X) \quad (2)$$

where $X = [F]/[H]$ the ratio of the concentration of **F** and **H** in the monomer feed. Figure 5 shows the diagrams of the statistical distribution of **F**-centered triads along the copolymer chains, as function of the ratio of molar concentration of both monomers in the feed. As expected the **HFH** triad molar fraction decreases drastically whereas the molar fraction of homotriads **FFF** increases smoothly, with increasing **X**. However, the molar fraction of heterotriads having one **H** unit, $FFH^+ = FFH + HFF$, reaches a maximum of 0.5 for $X = 1.0$.

### Thermal Transitions of F–H Copolymers

The glass transition temperature of poly(2-hydroxyethyl methacrylate) was determined to be 358 K, as reported before.[24] However, no previous report has been made of the glass transition temperature of poly(furfuryl acrylate), and it turned out to be 321 K, according to the experimental conditions of this work.

Considering the large difference between the glass transition temperature of **F** and **H** homopolymers, we thought that it could be of interest to analyze the glass transition of the copolymers prepared, as well as the variation of T_g with the composition of the copolymer system. In this way, Figure 6 shows the variation of the glass transition temperature of the copolymers with the composition of the macromolecular chains expressed as the average weight fraction of **F**, W_F. A monotonic decrease of T_g is observed increasing the **F** weight fraction in the copolymer system, the T_g of copolymers being between the corresponding homopolymers in the whole interval of compositions.

From a general point of view, assuming the dominance of the nearest neighbor interactions, the copolymer glass transition behavior would be determined by an additive contribution of the three comonomeric pairs in terms of diad sequences,[25] i.e., **FF**, **HH** and **FH**, or **HF**. In this sense, the microstructural effects on the glass transition of copolymer systems have successfully been considered by Johnston[26] and Barton.[27] The treatment proposed by Johnston is based on the "free volume theory" and can be considered an extension of the pioneer work of Fox et al.[28] In a recent publication[25] it has been suggested a linear expression of the Johnston's equation that can be written:

$$1/T_g - (W_F P_{FF}/T_{gFF}) - (W_H P_{HH}/T_{gHH})$$
$$= 1/T_{gFH}(W_F P_{FH} + W_H P_{HF}) \quad (3)$$

where T_g is the copolymer glass transition temperature, W_F and W_H the average weight fraction of monomer units **F** and **H** in the copolymer chains, T_{gFF} and T_{gHH} the glass transition temperatures of both homopolymers, and T_{gFH} that of the alternating copolymer; P_{FF}, P_{FH}, P_{HF}, and P_{HH} refer to the probabilities of having various linkages defined statistically according to eqs. (1) and (2). Figure 7 shows the linear diagram obtained after the appli-
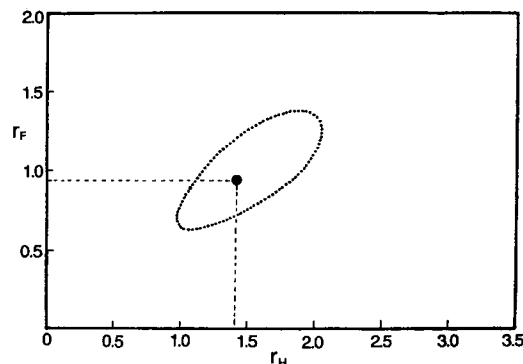
Figure 2. 95% confidence diagram for the reactivity ratios of **F** and **H**, determined by the nonlinear least-squares method suggested by Tidwell and Mortimer.
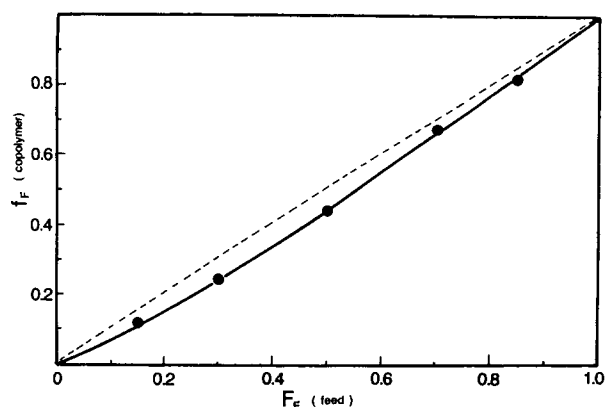
Figure 3. Composition diagram of the **F–H** copolymer system. The solid line corresponds to the theoretical diagram deduced from the reactivity ratios given in Table II.
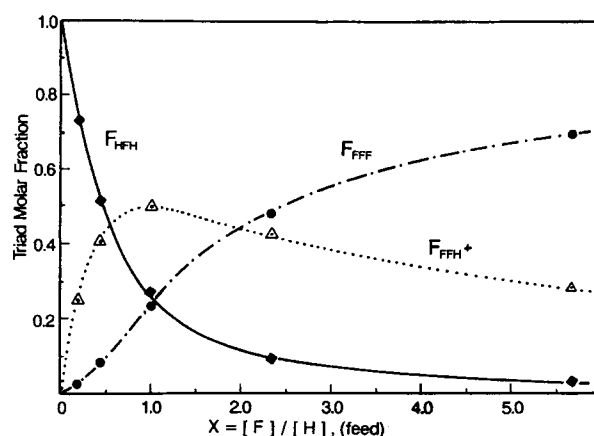

Figure 5. Variation of the molar fraction of furfuryl acrylate centered triads with the ratio of the concentration of monomers (X) in the feed.

cation of the experimental data to Johnston's treatment according to eq. (3). From the slope of the straight line a value of $T_{g\text{FH}}$ = 328 K was obtained.

However, Barton,[27] Uematsu and Honda,[29] and Hiroota and Kato[30] have proposed equations based on the "entropic theory," by extension of the pioneering suggestion of DiMarzio and Gibbs,[31] taking into consideration the T_g of both homopolymers and that of the alternating copolymer, $T_{g\text{FH}}$, together with the average composition and sequence distribution specified by the values of mole fraction of **FF**, **HH**, **FH**, and **HF** diads. The linear expression of Barton's equation can be written as:

$$T_g - (m_{\text{FF}}T_{g\text{FF}} + m_{\text{HH}}T_{g\text{HH}})$$

$$= (m_{\text{FH}} + m_{\text{HF}})T_{g\text{FH}} \quad (4)$$

with: $m_{\text{FF}} = m_{\text{F}}P_{\text{FF}}$, $m_{\text{FH}} = m_{\text{F}}P_{\text{FH}}$, $m_{\text{HH}} = m_{\text{H}}P_{\text{HH}}$, $m_{\text{HF}} = m_{\text{H}}P_{\text{HF}}$ where m_{F} and m_{H} are the molar frac-

tions of the monomeric units in the polymer chain. The linear diagram obtained after the application of the experimental data to eq. (4) is shown in Figure 8. The slope of the straight line obtained gives a value of $T_{g\text{FH}}$ = 326 K, in perfect agreement with the value obtained using Johnston's treatment.

Recently, Suzuki and Mathot[32] have suggested a new expression of Barton's equation that allows to estimate with minimum data the glass transition temperature of copolymer systems, by introducing the "run number" defined above, according to the following equation:

$$T_g = m_{\text{F}}T_{g\text{FF}} + m_{\text{H}}T_{g\text{HH}}$$

$$+ (R/R^*)[T_g(R^*) - T_{g1/2}] \quad (5)$$

where m_{F} and m_{H} are the molar fractions of monomer units in the copolymer chains, $T_{g\text{FF}}$ and $T_{g\text{HH}}$

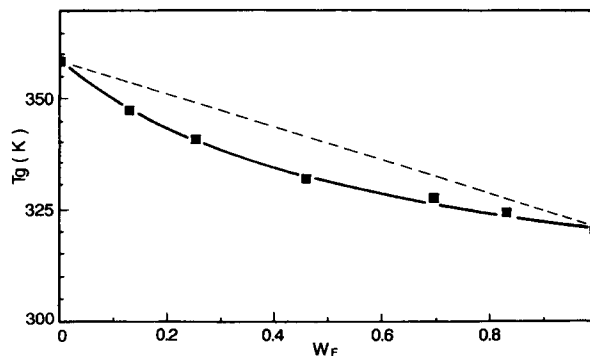**Figure 4.** Variation of the "run number" with the feed composition.

Figure 6. Glass transition temperature of **F–H** copolymers as a function of furfuryl acrylate weight fraction in the copolymer chains.
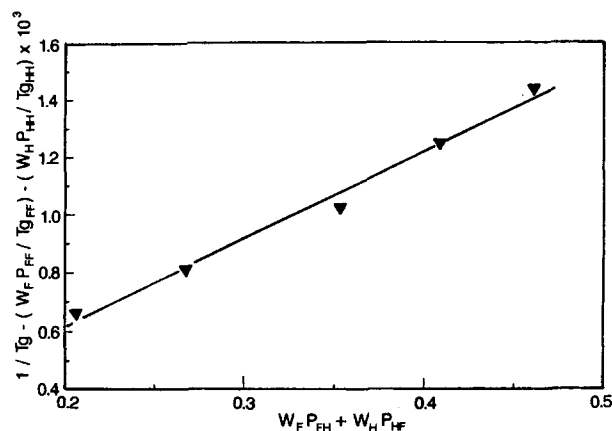
Figure 7. Application of the linearized expression of Johnston's treatment to the copolymer system **F–H**.

the glass transition temperatures of the corresponding homopolymers, R the run number, R^* the value of R for $m_F = m_H = 0.5$, $T_g(R^*)$ the glass transition temperature of an equimolecular random copolymer, and $T_{g1/2}$ the average arithmetical value of the T_g of both homopolymers, i.e., $T_{g1/2} = \frac{1}{2}(T_{gFF} + T_{gHH})$. If the T_g of copolymer samples is plotted against R, the diagram drawn in Figure 8 is obtained, where the dotted elliptical line corresponds to the prediction of eq. (5) and the straight line corresponds to the middle point of the T_g values predicted for random copolymers at a given value of R. A significant algebraic characteristic of this line is that the extrapolation at $R = 0$ gives the value of $T_{g1/2}$, whereas the extrapolation at $R = 100$ provides the T_{gFH}. The value obtained from the diagram shown in Figure 9 is $T_{gFH} = 325$ K, which is very close to those obtained by the application of the linear expressions of the treatments of Johnston and Barton.
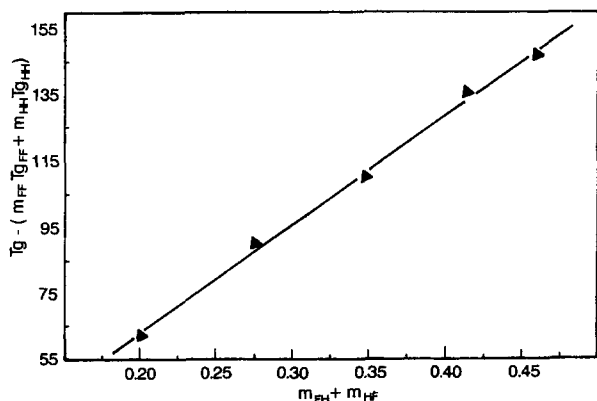

Figure 8. Application of the linearized expression of Barton's treatment to the copolymer system **F–H**.
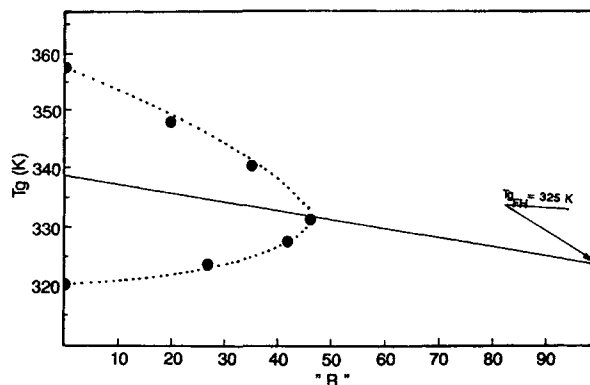

Figure 9. Variation of T_g with the "run number" for F–H copolymers, according to the treatment of Suzuki and Mathot.

It is clear from these values that the alternating diad **FH** or **HF** presents a glass transition temperature lower than the arithmetical average of the T_g of both homopolymers. The physical significance of this result is that the alternating diad presents a higher flexibility than the expected from the combination of both kinds of monomeric units, according to the glass transition temperatures of the corresponding homopolymers. It is interesting to stress that the value of T_{gFH} is rather close to T_{gFF}, which would indicate that the intra- or intermolecular interactions between aromatic side groups of polymeric chains are the main controlling elements of the thermal behavior of this copolymerization system.

These results evidence that the three models tested (Johnston, Barton, as well as modified Barton diad models) describe satisfactorily the dependence of copolymer T_g on the composition and sequence distribution of the F–H system. Also, an interesting conclusion is that the T_g of pure poly(furfuryl acrylate) has been determined unambiguously by two different ways: the experimental determination of an exhaustively dried polymer sample, giving a value of 321 K and that of the extrapolation of the diagram drawn in Figure 5 to $W_H = 0$, which correspond to the same value, with a minimum experimental error. It is noteworthy that the T_{gFF} is rather close to the T_g of phenyl, 2-chlorophenyl, and 4-chlorophenyl poly(acrylate)s,[25] which means that the dipolar interactions of the side aromatic rings, compensate the increase in the flexibility of the side group associated with the introduction of the methylene group in the furfuryl acrylate units, compared with the aforementioned phenyl derivatives.

REFERENCES AND NOTES

1. A. Gandini, *Adv. Polym. Sci.*, **25**, 47 (1977).
2. C. E. Rehberg and C. H. Fisher, *J. Org. Chem.*, **12**, 226 (1947).
3. M. Mihajlov and H. Boudevska, *Makromol. Chem.*, **177**, 80 (1968).
4. M. Mihajlov, H. Boudevska, and A. A. Berlin, *C. R. Acad. Bulg. Sci.*, **19**, 807 (1966).
5. J. C. Bevington and D. O. Harris, *J. Polym. Sci. Polym. Lett. Ed.*, **5**, 799 (1967).
6. M. P. Patel and M. Braden, *Biomaterials*, **12**, 645 (1991).
7. M. P. Patel and M. Braden, *Biomaterials*, **12**, 649 (1991).
8. D. Zaldívar, C. Peniche, A. Bulay, and J. San Román, *Polymer*, in press.
9. T. Okano, M. Katayama, and I. Shinohara, *J. Appl. Polym. Sci.*, **22**, 369 (1978).
10. M. S. Payne and T. A. Horbett, *J. Biom. Mat. Res.*, **21**, 843 (1987).
11. N. Nishioka, K. Kosai, and M. Uno, *Polymer*, **30**, 182 (1989).
12. A. Rembaun, S. P. S. Yen, E. Cheong, S. Wallace, R. S. Molday, I. L. Gordon, and W. J. Dreyer, *Macromolecules*, **9**, 328 (1976).
13. J. C. Meslard, L. Yean, F. Subira, and J. P. Vairon, *Makromol. Chem.*, **187**, 787 (1986).
14. M. Szycher, Ed., *Biocompatible Polymers, Metals and Composites*, Technomic, Lancaster, PA, 1983.
15. F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).
16. P. W. Tidwell and G. A. Mortimer, *J. Polym. Sci. A*, **3**, 369 (1965).
17. M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
18. T. Kelen and F. Tüdös, *J. Macromol. Sci. Chem. A*, **9**, 1 (1975).
19. D. W. Behnken, *J. Polym. Sci. A*, **2**, 645 (1964).
20. J. F. Bork and L. E. Coleman, *J. Polym. Sci.*, **43**, 413 (1960).
21. M. Orbay, R. Laible, and L. Dulog, *Makromol. Chem.*, **47**, 183 (1982).
22. H. J. Hardwood and W. M. Ritchey, *J. Polym. Sci.*, **B2**, 601 (1964).
23. J. L. Koenig, *Chemical Microstructure of Polymer Chains*, Wiley, New York, 1980.
24. J. San Román, B. Levenfeld, E. L. Madruga, and J. P. Vairon, *J. Polym. Sci. Part A: Polym. Chem.*, **29**, 1023 (1991).
25. J. San Román, E. L. Madruga, and J. Guzmán, *Polym. Comm.*, **25**, 373 (1984).
26. N. W. Johnston, *J. Macromol. Sci. Rev. Macromol. Chem.*, **C14**, 215 (1976).
27. J. M. Barton, *J. Polym. Sci. C*, **30**, 573 (1970).
28. T. G. Fox, *Bull. Am. Phys. Soc.*, **1**, 123 (1956).
29. I. Uematsu and K. Honda, *Rep. Prog. Polym. Phys. Jpn.*, **8**, 111 (1965).
30. M. Hirooka and T. Kato, *J. Polym. Sci. B*, **12**, 31 (1974).
31. E. A. DiMarzio and J. H. Gibbs, *J. Polym. Sci.*, **40**, 121 (1959).
32. H. Suzuki and V. B. F. Mathot, *Macromolecules*, **22**, 1380 (1989).