Free radical copolymerization of furfuryl methacrylate and *N*-vinylpyrrolidone

Dionisio Zaldívar and Carlos Peniche*
*Laboratorio de Materiales Sintéticos (LMS) and *Facultad de Química, Universidad de La Habana, 10400 Havana, Cuba*

and Anna Bulay
NPO 'Plastmassi', Petrovskyi Proezd 35, 111 112 Moscow, Russia

and Julio San Román†
Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain
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Copolymers of furfuryl methacrylate (F) and *N*-vinylpyrrolidone (P) were prepared by free radical polymerization in *N*,*N*-dimethylformamide solution at 50°C, using 2,2'-azobisisobutyronitrile 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 non-linear least-squares treatment. The reactivity ratios obtained were $r_F = 3.92$ and $r_P = 0.004$. The microstructure of the copolymer chains is described on the basis of first-order Markov statistics, and the copolymer glass transition temperatures (T_gs) were determined calorimetrically. The variation of T_g with 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 $T_g(F) = 392\,K$ and $T_g(P) = 358\,K$, whereas the T_g of the corresponding alternating diad has an average value of $T_{gFP} = 347\,K$.

(Keywords: copolymers; free radicals; reactivity ratios)

INTRODUCTION

The use of raw materials from renewable sources has been the focus of attention of a great number of scientific research groups all over the world during the last three decades. Compounds derived from 2-furfuraldehyde were extensively used during the 1960s and 1970s because of its accessibility from vegetable residues such as corn husks and sugar cane[1]. Although the pioneering work by Rehberg and Fisher[2] reports the formation of crosslinked polymers when furfuryl esters of acrylic and methacrylic acids were polymerized by free radical initiators, Mihajlov and Boudevska[3] demonstrated that when furfuryl methacrylate (F) or 5-carbomethoxyfurfuryl methacrylate were polymerized in bulk with free radical catalysts, insoluble crosslinked polymers were obtained. However, the polymerization in solution provided soluble polymers[4], and Bevington and Harris[5] reported the formation of soluble copolymers when F is copolymerized with methyl methacrylate in bulk (at low conversion), using 2,2'-azobisisobutyronitrile (AIBN) as the free radical initiator.

The use of polymeric systems based on acrylic derivatives as biomaterials for clinical applications has increased during the last two decades because of their excellent biocompatibility and long-term stability[6]. Many efforts have been directed towards the development of monomeric systems that on polymerization present lower shrinkage than the traditional methyl methacrylate. This characteristic seems to be connected with the molar volume of the corresponding compounds[7,8]. It has been demonstrated that large glassy molar volume methacrylates correspond to heterocyclic and cyclic derivatives, with a considerable effect on the glass transition temperature (T_g) of the corresponding polymers[9,10]. In this sense, Patel *et al.*[10,11] have successfully polymerized tetrahydrofurfuryl methacrylate for the preparation of dental filling materials and acrylic cements for orthopaedic surgery.

In the present paper, the free radical copolymerization of F with *N*-vinylpyrrolidone (P) is described. The election of P as comonomer results from the proved biocompatibility of the corresponding polymeric systems[6].

EXPERIMENTAL

Monomer preparation and purification of materials

F was prepared by transesterification of methyl methacrylate 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

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† To whom correspondence should be addressed

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gel 60 (Macherey-Nagel, Germany). The eluent was analysed by t.l.c. using Kieselgel 60 F 254 (Merck) as the stationary phase. The selected fraction was rotor evaporated in order to separate the solvent, and distilled.

P (supplied by Fluka) was distilled under reduced pressure and used without further purification.

AIBN was purified by fractional crystallization from methanol (m.p. 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 nitrogen pressure. Other reagents were of extra pure grade and used as purchased.

Copolymerization

Copolymerization reactions were performed in DMF solution at 50 ± 0.1°C in Pyrex glass ampoules sealed under high vacuum. The monomer and initiator concentrations were 1.0 and 1.5×10^{-2} mol l^{-1}, respectively. The sealed ampoules were shaken vigorously and immersed in a water bath maintained at the polymerization temperature. After reaction, the ampoules were removed from the bath and the contents were immediately 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 mixture of F and P were analysed by ^{1}H n.m.r. spectroscopy with a Bruker AM-200 spectrometer operating at 200 MHz. The spectra were recorded at 40°C on 5% (w/v) deuterated chloroform solutions.

Differential scanning calorimetry

The T_g values were determined with a Perkin-Elmer DSC-4 calorimeter. Measurements and calibration were carried out at a heating rate of 10°C min^{-1}. T_g was taken as the midpoint of the transition region. Samples (~40 mg) were introduced into the aluminium pan, heated at 450 K, compressed and then quenched at room temperature before carrying out the measurements. Measurements taken at heating rates of 5 and 15°C min^{-1} gave T_g values with a deviation of <2% with respect to those obtained at 10°C min^{-1}.

RESULTS AND DISCUSSION

The copolymerization of F with P in anhydrous DMF solutions was studied over a wide composition interval with molar fractions of F ranging from 0.01 to 0.50 in the monomer feed. The reaction time initially regulated to reach conversions of <5 wt% in order to satisfy the differential copolymerization equation[12]. The molar fraction of monomer units incorporated in the copolymer was determined from the ^{1}H n.m.r. spectra of copolymer samples prepared with different monomer feeds. The analysis was performed by comparing the integrated intensities of resonance signals with chemical shifts of 6.36δ assigned to the protons in positions 3 and 4 of the aromatic furfuryl ring and 3.10δ assigned to the protons in position 4 of the pyrrolidone ring. The data of molar composition of the initial mixtures of comonomers used and of the resulting copolymers are given in *Table 1*. It is interesting to stress here that it is very difficult (if not impossible) to prepare with accuracy and reproducibility copolymer samples with molar fractions of $f_F < 0.40$, since it would be necessary to use feeds with a F_F molar fraction of <0.002.

Table 1 Composition and conditional probability data of the free radical copolymerization of F and P in DMF solution at 50°C

F_F[a]	f_F[a]	Conversion (wt%)	P_{FP}	P_{PF}
0.010	0.43_0	2.5	0.965	0.716
0.020	0.52_1	3.1	0.926	0.836
0.050	0.53_4	3.0	0.829	0.929
0.100	0.56_0	3.5	0.697	0.965
0.150	0.60_1	2.9	0.591	0.978
0.200	0.64_2	3.8	0.505	0.984
0.300	0.72_3	2.3	0.373	0.991
0.400	0.80_1	3.7	0.277	0.994
0.500	0.87_3	3.8	0.203	0.996

[a] F_F and f_F are the molar fractions of F in the monomer feed and in the copolymer samples, respectively

Table 2 Copolymerization parameters of the free radical copolymerization of F with P

Method	r_F	r_P	$r_F \times r_P$	$1/r_F$	$1/r_P$
Fineman–Ross	5.40 ± 0.4	0.004 ± 0.020	0.022	0.19	250
Kelen–Tüdos	4.21 ± 1.6	0.007 ± 0.005	0.029	0.23	143
Tidwell–Mortimer	3.92	0.004	0.016	0.26	220

The reactivity ratios (*r* values) of the monomers were determined according to the general copolymer composition equation by applying the Tidwell and Mortimer non-linear least squares analysis[13]. To this end, initial approximated values of r_F and r_P were obtained by means of the Fineman–Ross[14] and Kelen–Tüdos[15] linearization methods. The results are shown in *Table 2*. It must be pointed out that although the r_F and r_P values obtained using the linearization methods are somewhat different, the same values are obtained when the non-linear least squares method is used. We stress here that the *r* values determined by the application of the analysis suggested by Tidwell and Mortimer[13] are the most probable values for this system. In this sense, the 95% confidence limit gives an idea of the experimental error and the accuracy of the experimental conditions used to generate the composition data[13]. 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 applying the mathematical treatment suggested by Behnken[16] and Tidwell and Mortimer[13]. The application of this treatment to the copolymerization data reported in *Table 1* and the *r* values quoted in *Table 2* provides the 95% confidence limits defined by the area of the elliptical diagram in *Figure 1*. This diagram confirms the excellent approximation of the r_F and r_P values as indicated by the reduced dimensions of the ellipse.

The average composition diagram shown in *Figure 2* has been drawn with the Tidwell and Mortimer r_F and r_P values using the Lewis–Mayo classical copolymerization equation; the experimental composition data

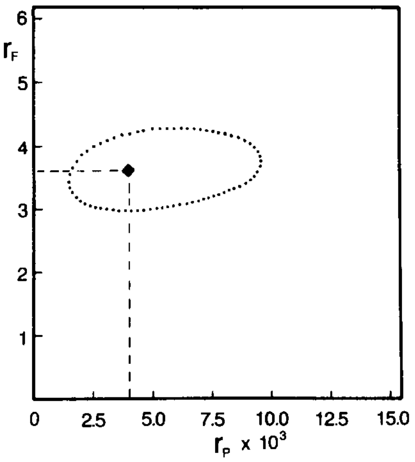

Figure 1 The 95% confidence diagram for the reactivity ratios of F and P, r_F and r_P, determined by the non-linear least-squares method suggested by Tidwell and Mortimer

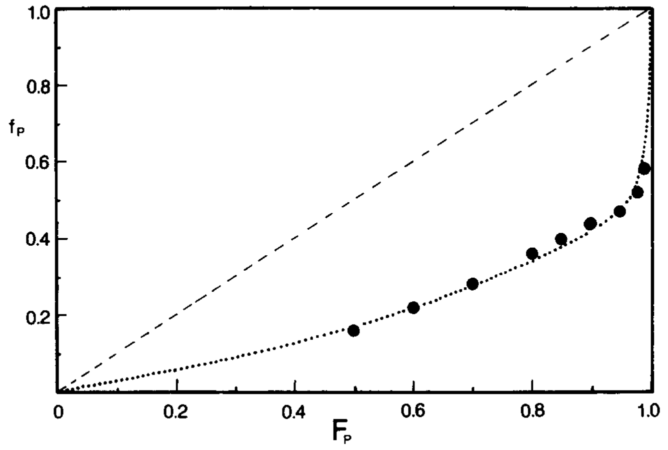

Figure 2 Composition diagram of the F–P copolymer system. The broken line corresponds to the theoretical diagram deduced from the r values given in *Table 2*

adequately fit the theoretical diagram represented by the broken line. The reactivity of growing radicals with F ends, as measured by the ratio $1/r_F$ is somewhat higher towards P than F monomer molecules. However, the reactivity of the growing radical with P ends is much higher towards F, in such a way that it can be considered that the growing radicals ending in a vinylpyrrolidone unit add exclusively an F molecule. The r values obtained for this copolymerization system are in the range of those reported for the free radical copolymerization of methyl methacrylate and vinylpyrrolidone[17,18].

From the values of r_F and r_P given in *Table 2* and taking into account well known statistical relationships, we have determined the 'run number', R, defined by Harwood and Ritchey[19] 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 r values and probability statistics for different values of F_F, covering a wide range of compositions. *Figure 3* shows the variation of R with F_F. The maximum value of $R(=89.3)$ is reached for a F_F of ~0.033. This is a result of the selectivity of addition for radicals ending with vinylpyrrolidone.

The statistical distribution of F centred triads was determined considering the equations for the first-order Markovian transition probabilities P_{FP}, P_{PF}, P_{FF} and P_{PP} according to the following equations[20]:

$$P_{FP} = 1 - P_{FF} = 1/(1 + r_F \cdot X) \qquad (1)$$

$$P_{PF} = 1 - P_{PP} = 1/(1 + r_P/X) \qquad (2)$$

where $X = [F]/[P]$ the ratio of the concentration of F and P in the monomer feed. *Figure 4* shows the statistical distribution of F centred triads along the copolymer chains as a function of X. As expected, the PFP triad molar fraction decreases drastically whereas the molar fraction of the FFF homotriad increases smoothly with increasing X. However, the molar fraction of heterotriads having one P unit, $FFP^+ = FFP + PFF$, reaches a maximum of 0.5 for $X = 0.25$.

Thermal transitions of F–P copolymers

The T_g of polyvinylpyrrolidone was determined to be 343 K, a value laying in the range of those reported in the literature[21]. However, no previous value has been given for the T_g of poly(furfuryl methacrylate), and it turned out to be 392 K.

Considering the large difference between the T_gs of F and P homopolymers, we thought that it could be of

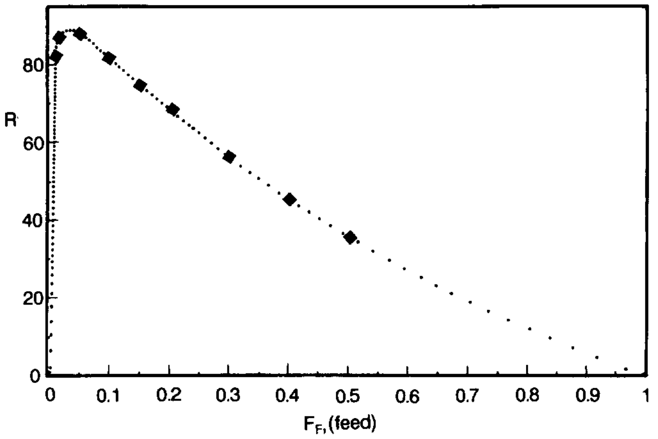

Figure 3 Variation of the 'run number' R with the feed composition F_F

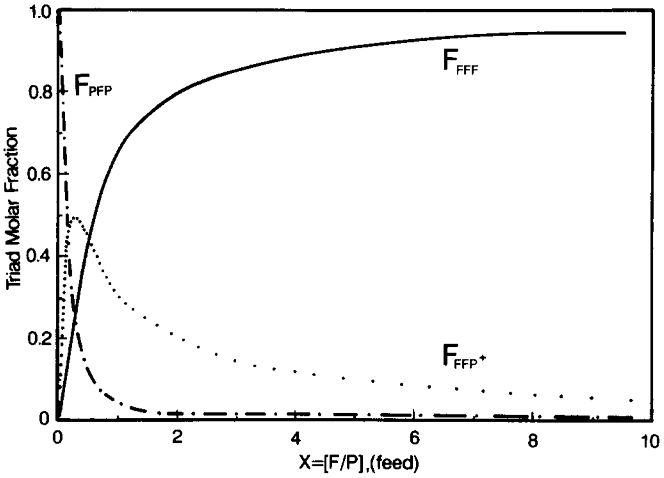

Figure 4 Variation of the molar fraction of F centred triads with the ratio of the concentration of monomers, X, in the feed

interest to analyse the glass transition of the copolymers prepared, as well as the variation of T_g with the composition of the copolymer. *Figure 5* shows the variation of the T_g of the copolymers with the composition of the macromolecular chains expressed as the average weight fraction of F, W_F. A monotonic increase in T_g is observed on increasing W_F in the copolymer system, the T_g of the copolymers being between the values for the corresponding homopolymers over the whole composition range.

From a general point of view, assuming the dominance of the nearest neighbour interactions, the copolymer glass transition behaviour would be determined by an additive contribution of the three comonomeric pairs in terms of diad sequences[22], i.e. FF, PP and FP or PF. In this sense, the microstructural effects on the glass transition of copolymer systems have been successfully considered by Johnston[23] and Barton[24]. The treatment proposed by Johnston is based on the 'free volume theory' and can be considered an extension of the pioneering work of Fox[25]. In a recent publication[22], it has been suggested that a linear expression of johnston's equation can be written as:

$$1/T_g-(W_FP_{FF}/T_{gFF})-(W_PP_{PP}/T_{gPP}) = 1/T_{gFP}(W_FP_{FP}+W_PP_{PF}) \quad (3)$$

where T_g is the glass transition temperature of the copolymer, W_F and W_P are the average weight fractions of monomer units F and P in the copolymer chains, T_{gFF} and T_{gPP} are the glass transition temperatures of both homopolymers, and T_{gFP} that of the alternating copolymer; P_{FF}, P_{FP}, P_{PF} and P_{PP} refer to the probabilities of having various linkages defined statistically according to equations (1) and (2). *Figure 6* shows the linear diagram obtained after the application of the experimental data to Johnston's treatment according to equation (3). From the slope of the straight line a value of $T_{gFP}=342$ K was obtained.

Barton[24], Uematsu and Honda[26] and Hirooka and Kato[27] have proposed equations based on the 'entropic theory', by extending the pioneering suggestion of DiMarzio and Gibbs[28], taking into consideration the T_g of both homopolymers and that of the alternating copolymer, T_{gFP}, together with the average composition and sequence distribution specified by the values of mole fractions of FF, PP, FP and PF diads. The linear expression of Barton's equation can be written as:

$$T_g-(m_{FF}T_{gFF}+m_{PP}T_{gPP})=(m_{FP}+m_{PF})T_{gFP} \quad (4)$$

with

$$m_{FF}=m_FP_{FF}; \qquad m_{FP}=m_FP_{FP}$$

$$m_{PP}=m_PP_{PP}; \qquad m_{PF}=m_PP_{PF}$$

where m_F and m_P are the molar fractions of the monomeric units in the polymer chain. The linear diagram obtained after the application of the experimental data to equation (4) is shown in *Figure 7*. The slope of the straight line obtained gives a value of $T_{gFP}=345$ K, in perfect agreement with the value obtained using Johnston's treatment.

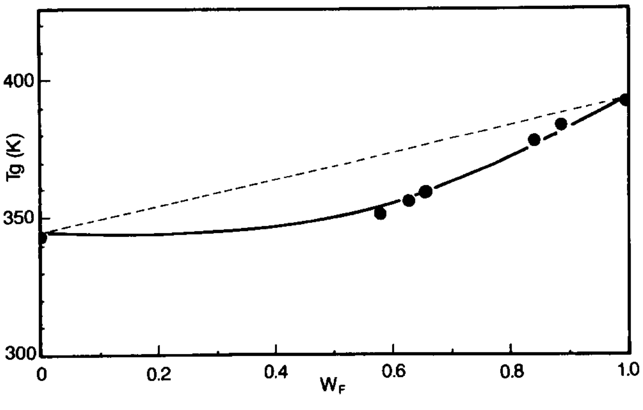

Figure 5 Glass transition temperature, T_g, of F–P copolymers as a function of the weight fraction of F, W_F, in the copolymer chains

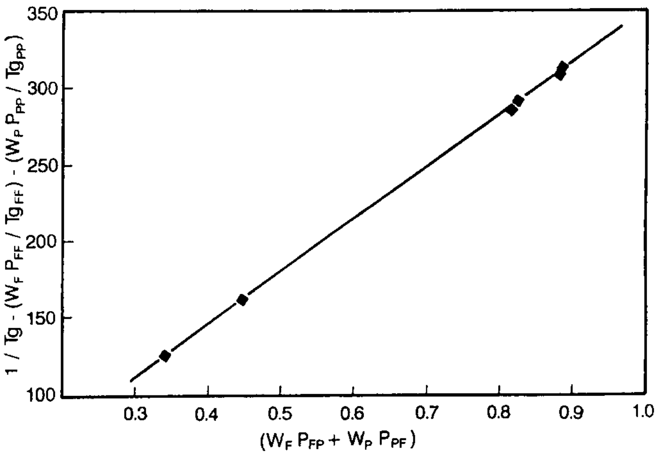

Figure 6 Application of the linearized expression of Johnston's treatment to the copolymer system F–P

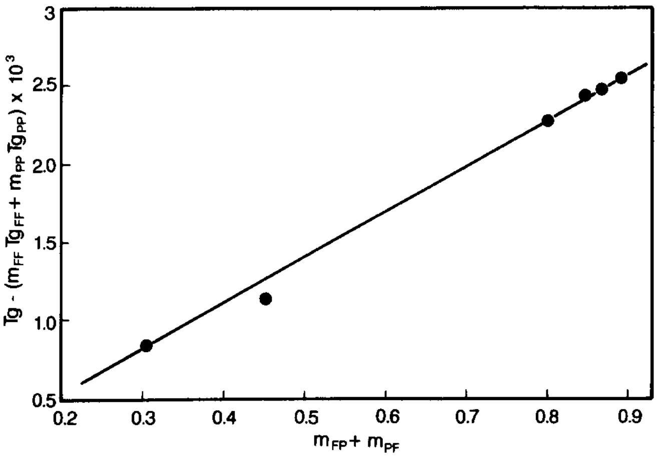

Figure 7 Application of the linearized expression of Barton's treatment to the copolymer system F–P

Recently, Suzuki and Mathot[29] have suggested a new expression for Barton's equation that allows the T_g of copolymer systems to be estimated with minimum data, by introducing R, defined above, according to the following equation:

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

where m_F and m_P are the molar fractions of monomer units in the copolymer chains, T_{gFF} and T_{gPP} are the glass transition temperatures of the corresponding homopolymers, R^* is the value of R for $m_F=m_P=0.5$, $T_g(R^*)$ is the glass transition temperature of an equimolecular random copolymer, and $T_{g1/2}$ is the average arithmetical value of the glass transition temperature of both homopolymers, i.e. $T_{g1/2}=\frac{1}{2}(T_{gFF}+T_{gPP})$. If the T_g of

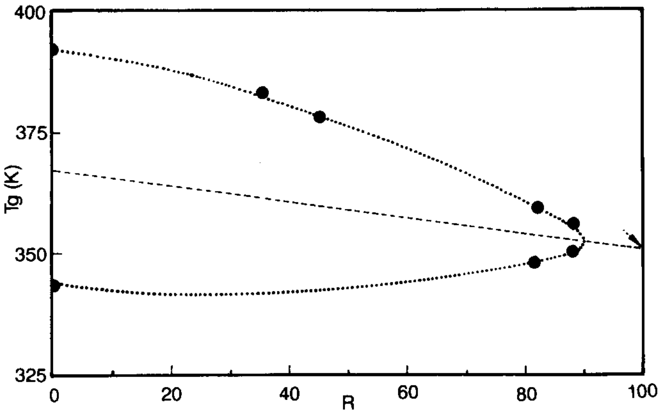

Figure 8 Variation of T_g with the 'run number' R for F–P copolymers. The elliptical line corresponds to the prediction of equation (5); the broken line corresponds to the mid values of T_g for each two points of the diagram with the same R, connecting $T_{g1/2}$ at $R=0$ and T_{gFP} at $R=100$. The value of T_{gFP} at $R=100$ is 351 K (indicated by an arrowhead)

copolymer samples is plotted against R, the diagram drawn in *Figure 8* is obtained, where the elliptical line corresponds to the prediction of equation (5) and the broken 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 T_{gFP}. The value obtained for T_{gFP} from *Figure 8* is 351 K, which is similar to the values obtained by applying the linear expressions of the treatments of Johnston and Barton.

It is clear from these values that the alternating diad FP or PF presents a $T_g < T_{g1/2}$. The physical significance of this result is that the alternating diad presents a higher flexibility than that expected from the combination of both kinds of monomeric units, according to the T_gs of the corresponding homopolymers.

These results are evidence that the three models tested (the Johnston, the Barton and the modified Barton diad models) describe satisfactorily the dependence of copolymer T_g on the composition and sequence distribution of the F–P system. Also, an interesting conclusion is that the T_g of pure poly(furfuryl methacrylate) has been determined unambiguously in two different ways: the experimental determination of an exhaustively dried polymer sample giving a value of 392 K, and that of the extrapolation of the diagram drawn in *Figure 5* to $W_P = 0$, which corresponds to the same value, with a minimum experimental error.

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