Synthesis, Reactivity Ratios, and Solution Behavior of Vinylpyrrolidone-*co*-Monoalkyl Itaconate and Vinylpyrrolidone-*co*-Dialkyl Itaconate Copolymers

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ABSTRACT: Copolymers containing vinylpyrrolidone and mono and dialkyl itaconate units with different length in the side chains were synthesized and characterized. Copolymers of vinylpyrrolidone with three different compositions of monomethyl, monoethyl, monopropyl, monoamyl, dimethyl, diethyl, dipropyl, and diamyl itaconate were obtained by radical polymerization. The reactivity ratios was estimated by using the classical Fineman−Ross and Kelen Tüdos procedures. These parameters were also estimated using a computer program based on nonlinear minimization algorithm, starting from the values of r_1 and r_2 obtained by the linear procedures. The copolymers can be considered as random. Fractionation of the copolymers were achieved by fractional precipitation. Fractions were characterized by viscometry and light scattering measurements. The unperturbed dimensions were determined using the Stockmayer−Fixman method. Higher rigidity indexes and characteristic ratios are observed in copolymers containing diitaconate units than that with monoitaconate moieties. The dependence of the glass transition temperature T_g with copolymer composition and its correlation with the chain stiffness is also analyzed.

Introduction

Poly(itaconates) may be considered as typical comb-like polymers, depending on the length of the side chain.[1] The effect of the length of the side chain and the presence of the free carboxylic group have been taken into account to explain the particular conformational behavior of some poly(monoitaconates).[1] Radical polymerization of several monomers bearing two functional chemical groups has been studied.[2,3] The cooperative effect of the different groups has been also analyzed.[3b] On the other hand, poly(di-*n*-alkyl itaconates) obtained from diesters of itaconic acid and lower unbranched alcohols show important changes in both solution and the solid state properties.[4−6] The thermal stability and dielectric and viscoelastic properties of members of several series of poly(itaconates) have been assessed by several authors.[7−10]

The thermodynamic and conformational behavior of poly(itaconates) in general has been extensively studied;[1c,11−13] nevertheless, the effect of the polymer chemical structure and its influence in this behavior is not yet clearly understood. The high rigidity of poly(monoitaconates) in comparison with that of poly(diitaconates) has been attributed mainly to the free carboxylic group. In the case of poly(di-*n*-alkyl itaconates), with $n > 6$ there is an important increase in the steric hindrance because of the presence of two side groups per repeating unit. Therefore, motions corresponding to these groups will be inhibited as a whole due to the presence of adjacent substituents.

Our previous background in poly(mono- and diesters) derived from itaconic acid[1c,14] allows us to perform a systematic study of the family of poly(itaconates) with linear or branched substituents in the side chain in order to get a generalization about the conformational and relaxation properties in this important class of polymers.[6,14]

Copolymers containing itaconate units should be very interesting because they have the capacity to undergo strong interactions. Depending on the structure of the comonomer, it is possible to vary the intramolecular interactions between unlike units, which influence short- as well as long-range interactions. On the other hand, vinylpyrrolidone (VP) is a monomer frequently used as a comonomer,[11a,15−18] mainly because of its amphiphilic character. In fact, vinylpyrrolydone contains a highly polar amide group which confers hydrophilic and polar-attracting properties. The apolar methylene and methine groups in the backbone and the ring confer hydrophobic properties.[19]

Copolymers of vinylpyrrolidone and monoalkyl itaconates with long side chains were previously reported and their solution behavior and rigidity indexes were established.[11a] Random copolymers with a tendency to alternate were described. The effect of the comonomer unit on the solution behavior of the copolymer, relative to the corresponding poly(monoitaconates), was analyzed.

In this work we have studied the effect of the side-chain length of mono- and diitaconates copolymerized with vinylpyrrolidone. In order to clarify this effect on the solution behavior and on the unperturbed dimension of the copolymers, we have determined the conformational and viscometric parameters. In this work we present the synthesis and characterization of copolymers of vinylpyrrolidone and the first members of the series of monoitaconates (MI) and diitaconates (DI), i.e., monomethyl (MMI), monoethyl (MEI), monopropyl (MPI), monoamyl (MAI), dimethyl (DMI), diethyl (DEI), dipropyl (DPI), and diamyl (DAI) itaconate. The determination of the reactivity ratios r_1 and r_2 of the copolymers should be performed in order to estimate the copolymer sequence.

Experimental Section

Monomer and Copolymer Preparation. Monoitaconates were prepared by esterification of itaconic acid with the corresponding alcohols using acetyl chloride as catalyst as reported previously.[1c,20,21] Monomers were purified by recrystallization from petroleum ether.

Diitaconates were obtained by conventional acid-catalyzed esterification of itaconic acid with the corresponding alcohols

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using *p*-toluenesulfonic acid in toluene.[22] The pure monomers were obtained by repeated distillation of the crude product under reduced pressure. Purity was confirmed by ^{1}H NMR and Fourier transform infrared (FTIR) spectroscopy. A commercial sample of vinylpyrrolidone from Aldrich previously distilled under reduced pressure was used in the copolymerization process.

Radical copolymerization of the monomers was carried out in bulk 340−350 K (depending on the monomer used) under nitrogen, using α,α′-azobisisobutyronitrile (AIBN) as the initiator. The monomer feed ratio was varied in a series of copolymerizations as shown in Table 1. Polymerization time was varied from 15 to 60 min, and the conversion of monomer to polymers was always about 10%. Purification of the copolymers was achieved by repeated reprecipitation with diethyl ether before vacuum drying at 313 K.

Copolymer Characterization. Compositions of the copolymers were determined by FTIR measurements in KBr using a Bruker IFS 25 spectrophotometer, with 526 accumulations for each sample. Peaks at 1730 and 1694 cm^{-1} corresponding to the vibrations of the carbonyl groups of monoitaconate and vinylpyrrolidone, respectively, were analyzed. ^{1}H NMR spectra were recorded in a Bruker AC-200 spectrometer using TMS as an internal standard and deuterated dimethyl sulfoxide as solvent. The weight-average molecular weight ($\bar{M}_w$) of the fractions were determined by static light scattering (SLS) measurements using a Dawn-F light scattering instrument from Wyatt Technology containing 15 permanently mounted detectors and a He−Ne laser at $\lambda = 632.8$ nm. Polydispersity indexes ($\bar{M}_w/\bar{M}_n$) of the fractions were determined by size exclusion chromatography (SEC) using a Perkin-Elmer high-performance liquid chromatograph equipped with a 6000 psi pump, a Perkin-Elmer differential refractometer (Model LC-25) and a 175-μL injector. Three Waters Associates Ultra Styragel columns connected in series were used (10^3, 10^4, 10^5 Å). Samples were eluted with tetrahydrofuran (THF), at a speed of 1 mL min^{-1} at room temperature. The analysis of the elution data was performed according to the Rabek[23] treatment of the data using a computer program based on the normalization of the chromatograms. All solvents were Merck analytical grade. Copolymers of different compositions were fractionated by standard precipitation procedures using ethanol as solvent and petroleum ether as precipitant. The variation of the copolymer composition of the fractions relative to the initial copolymer is 2% in average. Viscosity measurements at 298 K were performed with a Desreux−Bischoff dilution viscometer[24] with negligible kinetic energy corrections. Intrinsic viscosity [η] was determined by the usual extrapolations according to the classical Huggins and Kraemer relations.

Results and Discussion

Monomer Reactivity Ratios. The monomer reactivity ratios r_1 and r_2 were determined by the least-squares method according to Fineman and Ross[25] (FR) equation:

$$G = Fr_1 - r_2 \tag{1}$$

and/or

$$G/F = -r_2(1/F) + r_1 \tag{2}$$

where the transformed variables are

$$G = x(y-1)/y \quad \text{and} \quad F = x^2/y \tag{3}$$

x and y are defined as

$$x = M_1/M_2 \quad \text{and} \quad y = \mathrm{d}M_1/\mathrm{d}M_2 \tag{4}$$

where M_1 and M_2 are the concentration of monomers and $\mathrm{d}M_1/\mathrm{d}M_2$ corresponds to the concentration ratio of the copolymer components. Values of r_1 and r_2 obtained from the FR procedure are summarized in Table 2 as

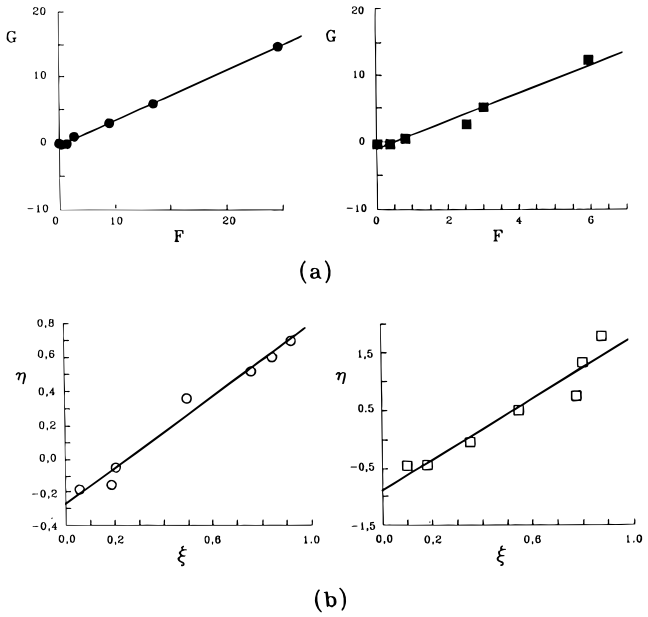

Figure 1. (a) FR representation of the copolymerization parameters for (●) MAI-*co*-VP and (■) DMI-*co*-VP. (b) KT representation of the copolymerization parameters for (○) MAI-*co*-VP and (□) DMI-*co*-VP.

FR_1 and FR_2, where the feed and copolymer composition is expressed in mole percent of VP (FR_1) and mole percent of MI or DI (FR_2), respectively. The obtained values of r_1 and r_2 using FR_1 and FR_2 are generally different,[11a,26] which is one of the weaknesses of the method.

r_1 and r_2 were also determined by the Kelen−Tüdös[27] (KT) treatment, according to the equation

$$\eta = (r_1 + r_2/\alpha)\,\xi - r_2/\alpha \tag{5}$$

where η and ξ are mathematical functions of the mole ratios of monomers in the feed and in the copolymer, defined as[21]

$$\eta = G/(\alpha + F) \quad \text{and} \quad \xi = F/(\alpha + F) \tag{6}$$

and α denotes an arbitrary constant, which according to the authors[27] has a best value of $\alpha = (F_m F_M)^{1/2} > 0$, where F_m and F_M are the lowest and highest value of the calculated F from the series of measurements. Plotting the η values calculated from the experimental data as a function of ξ, straight lines are obtained, which extrapolated to $\xi = 0$ and $\xi = 1$ gives $-(r_2/\alpha)$ and r_1 (both as intercepts). Parts a and b of Figure 1 respectively represent the FR and KT plots for MAI-*co*-VP and DMI-*co*-VP copolymers as an example of this kind of representation. Similar plots are obtained for all the copolymeric systems studied with correlations R^2 up to 0.950. Table 1 summarizes the copolymerization data for copolymers containing MMI, MEI, MPI, MAI, DMI, DEI, DPI, and DAI with VP: composition in feed, copolymer composition, and the x, y, G, F, η, ξ, and α parameters according to eqs 3−6. Despite the extent of the experimental error in y and therefore in the other parameters, three significant digits (as written in Table 1) are taken into account for the calculations. These methods correspond to the so-called straight-line intersection methods, and poor agreement is found for the determination of r_1 and r_2 for the different copolymers as summarized in Table 2. Copolymers containing MI units follow a classical behavior for radical copolymerizations in the

Table 1. Copolymerization Data for Copolymers Containing MMI, MEI, MPI, MAI, DMI, DEI, DPI, and DAI with VP: Composition in Feed, Resulting Composition in the Copolymer, Ratio of Monomer Concentration (*x*), Concentration Ratio of the Copolymer Components (*y*), Fineman and Ross Parameters *G* and *F*, and Kelen−Tüdos Parameters η, ξ, and α

[VP] feed (mol %)	[VP] copolym. (mol %)	*x*	*y*	*G*	*F*	η	ξ
			MMI/VP ($\alpha = 1.91$)				
0.111	0.087	0.144	0.113	−0.300	0.184	−0.540	0.088
0.250	0.205	0.324	0.266	−0.894	0.218	−0.388	0.171
0.667	0.538	0.865	0.699	−0.372	1.070	−0.125	0.360
1.000	0.923	1.297	1.197	0.213	1.410	0.064	0.424
2.333	2.030	3.027	2.633	1.877	3.480	0.314	0.599
4.000	3.762	5.189	4.880	4.126	3.950	0.555	0.742
9.000	5.250	11.670	6.811	9.950	19.820	0.455	0.913
			MEI/VP ($\alpha = 1.83$)				
0.053	0.053	0.075	0.075	−0.925	0.075	−0.498	0.039
0.250	0.190	0.355	0.271	−0.955	0.465	−0.416	0.203
0.429	0.351	0.610	0.500	−0.610	0.744	−0.237	0.289
1.000	1.041	1.423	1.481	0.462	1.367	0.145	0.428
3.000	2.571	4.270	3.660	1.529	4.981	0.456	0.731
5.667	5.250	8.070	7.473	6.990	8.715	0.663	0.826
19.000	11.500	27.050	16.370	25.390	44.690	0.545	0.961
			MPI/VP ($\alpha = 0.965$)				
0.053	0.087	0.082	0.135	−0.525	0.050	−0.517	0.049
0.176	0.220	0.273	0.340	−0.530	0.219	−0.447	0.185
0.429	0.370	0.664	0.573	−0.495	0.770	−0.285	0.444
1.000	0.818	1.550	1.268	0.328	1.895	0.115	0.650
1.857	1.500	2.877	2.324	1.639	3.561	0.362	0.787
4.000	2.571	6.198	3.990	4.642	9.640	0.438	0.909
9.000	6.692	13.940	10.370	12.600	18.730	0.639	0.951
			MAI/VP ($\alpha = 1.37$)				
0.111	0.176	0.200	0.425	−0.270	0.094	−0.185	0.060
0.250	0.351	0.450	0.633	−0.261	0.320	−0.154	0.189
0.429	0.493	0.772	0.880	−0.105	0.680	−0.051	0.209
1.000	1.273	1.801	2.29	1.015	1.420	0.364	0.508
2.333	2.125	4.204	3.820	3.103	4.963	0.518	0.772
4.000	3.350	7.207	6.030	6.011	8.610	0.602	0.862
9.000	7.333	16.210	13.210	14.980	19.900	0.698	0.936
			DMI/VP ($\alpha = 0.697$)				
0.111	0.220	0.158	0.312	−0.348	0.080	−0.448	0.103
0.176	0.282	0.251	0.401	−0.375	0.157	−0.438	0.184
0.429	0.667	0.610	0.950	−0.320	0.390	−0.029	0.359
1.000	1.632	1.423	2.320	0.387	0.873	0.516	0.563
2.333	3.000	3.320	4.270	2.542	2.580	0.775	0.787
4.000	7.333	5.690	10.430	5.140	3.104	1.353	0.817
9.000	19.000	12.810	27.040	12.330	6.070	1.820	0.897
			DEI/VP ($\alpha = 0.68$)				
0.111	0.250	0.186	0.420	−0.257	0.082	−0.337	0.110
0.250	0.449	0.420	0.753	−0.138	0.234	−0.151	0.256
0.429	0.613	0.718	1.027	0.019	0.502	0.004	0.425
1.000	1.500	1.675	2.510	1.007	1.118	0.560	0.622
2.333	3.550	3.909	5.940	3.250	2.572	0.999	0.791
4.000	8.090	6.700	13.550	6.205	3.310	1.554	0.830
9.000	24.000	15.080	40.210	14.700	5.65	2.320	0.893
			DPI/VP ($\alpha = 1.21$)				
0.111	0.220	0.214	0.423	−0.292	0.108	−0.221	0.082
0.250	0.429	0.482	0.826	−0.102	0.281	−0.068	0.189
0.429	0.538	0.826	1.038	0.030	0.657	0.016	0.352
1.000	1.174	1.928	2.263	1.076	1.643	0.377	0.576
2.333	3.545	4.498	6.835	3.840	2.960	0.921	0.710
4.000	4.555	7.712	8.783	6.834	6.772	0.856	0.848
9.000	11.500	17.351	22.170	16.560	13.580	1.148	0.918
			DAI/VP ($\alpha = 1.52$)				
0.111	0.190	0.270	0.463	−0313	0.157	−0.187	0.094
0.250	0.389	0.608	0.946	−0.071	0.390	−0.018	0.205
0.429	0.563	1.042	1.368	0.280	0.794	0.121	0.343
1.000	1.325	2.432	3.224	1.677	1.835	0.500	0.547
2.333	2.846	5.675	6.923	4.855	4.652	0.787	0.754
4.000	7.330	9.730	17.840	9.185	5.300	1.345	0.777
9.000	13.280	21.890	32.320	21.210	14.830	1.297	0.907

sense that $r_1 < 1$ and $r_2 < 1$. Nevertheless, for copolymers containing DI units, higher values of the reactivity ratios are observed mainly for r_1. In the particular case of DEI-*co*-VP copolymer, the high r_1 and r_2 values obtained by the FR method are unexpected for radical copolymerization. Therefore, in this case it should be considered a copolymer with some tendency toward block formation. Differences in the values of the reactivity ratios obtained by both methods are expected according to data generally reported,[11a,26,27] and gross

Table 2. Monomer Reactivity Ratios r_1 and r_2 and the Product r_1r_2 obtained by Fineman−Ross (FR_1, FR_2) and Kelen−Tüdos (KT) Methods for Copolymers Containing MMI, MEI, MPI, MAI, DMI, DEI, DPI, and DAI with VP

copolymer	method	r_1	r_2	r_1r_2
MMI−VP	FR_1	0.53	0.21	0.11
	FR_2	0.89	0.61	0.54
	KT	0.76	1.12	0.85
	NLMA	1.14	1.19	1.35
MEI−VP	FR_1	0.60	0.60	0.36
	FR_2	0.98	0.89	0.87
	KT	0.77	1.04	0.80
	NLMA	0.78	1.07	0.85
MPI−VP	FR_1	0.69	0.93	0.64
	FR_2	0.55	0.42	0.23
	KT	0.59	0.66	0.39
	NLMA	0.46	0.59	0.27
MAI−VP	FR_1	0.77	0.42	0.32
	FR_2	0.53	0.82	0.43
	KT	0.77	0.37	0.29
	NLMA	0.84	0.54	0.45
DMI−VP	FR_1	2.10	1.20	2.52
	FR_2	0.50	1.51	0.76
	KT	1.70	0.61	1.04
	NLMA	1.30	0.50	0.65
DEI−VP	FR_1	2.60	1.50	3.90
	FR_2	0.41	1.60	0.67
	KT	2.01	0.65	1.31
	NLMA	1.12	0.37	0.41
DPI−VP	FR_1	1.24	0.61	0.76
	FR_2	0.36	0.86	0.31
	KT	1.21	0.51	0.62
	NLMA	0.92	0.39	0.36
DAI−VP	FR_1	1.50	0.70	1.05
	FR_2	0.54	1.34	0.72
	KT	1.47	0.67	0.98
	NLMA	1.12	0.49	0.55

inaccuracies have been well documented[28,29] in the use of linear estimation methods. The main disadvantage of these linear methods is the use of statistically invalid assumptions.[29] Reactivity ratios are nowadays usually estimated by using procedures based on the statistically valid error-in-variables model (EVM).[28,29] In order to gain confidence about the reactivity ratios of moalkyl itaconate-*co*-vinylpyrrolidone and dialkyl itaconate-*co*-vinylpyrrolidone copolymers, these parameters were also estimated using a computer program based on the nonlinear minimization algorithm (NLMA), starting from the values of r_1 and r_2 obtained by the Finemann−Ross[25] and Kelen−Tüdos[27] procedures. These linear methods can be used to at least obtain "good initial" r_1 and r_2 estimation.[28] Table 2 also summarizes the r_1 and r_2 values obtained using NLMA. Figure 2 shows the 95% posterior probability contours for estimated r_1 and r_2 starting from FR_1, FR_2, and KT values taken from Table 2 for MEI−VP and MPI−VP, as representative examples of the NLMA method for the probability contour. Similar contours are obtained for all the copolymers studied. The obtained r_1 and r_2 values were generated using errors of 1% for the monomer feed composition and 5−7% for the copolymer composition, depending on the system analyzed.

The results shown in Table 2 indicate a qualitative discrepancy among the different methods used to obtain r_1 and r_2. Nevertheless, irrespective of the method for determining r_1 and r_2, in general the systems can be considered as random copolymers. This result is in a qualitative agreement with the ^{1}H NMR spectra. This is an interesting result for the analysis of the solution behavior of these materials, because the resulting copolymer should have a random distribution of flexible VP units.

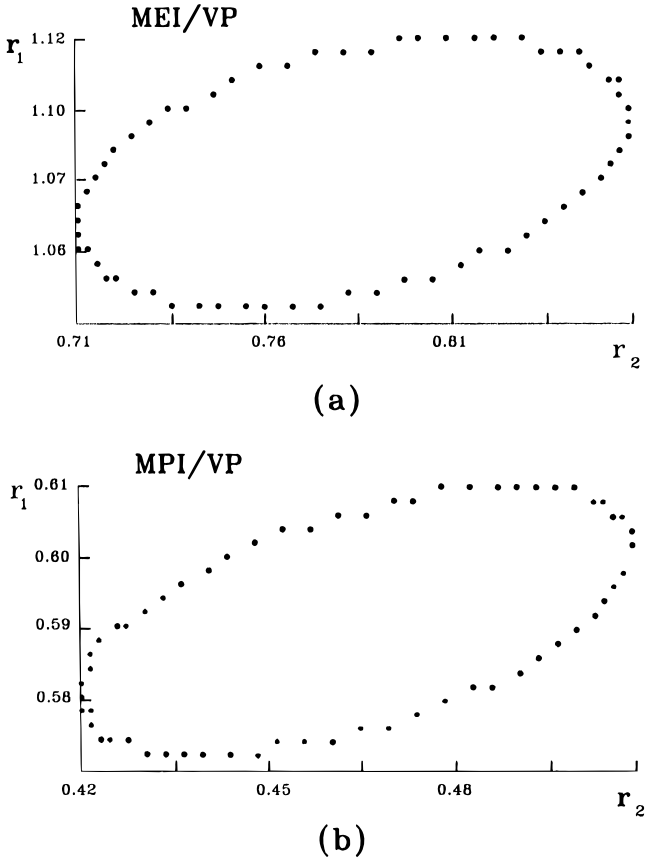

Figure 2. The 95% posterior contour for estimated r_1, r_2. (a) MEI-*co*-VP and (b) MPI-*co*-VP.

Solution Behavior. To analyze the effect of inserting comonomers on the solution behavior of poly(mono- and diitaconates), a viscometric study of fractions of the different copolymers at three different compositions was performed. Copolymers selected for the present study contains approximately 20, 50, and 80% VP (mol %), respectively. The true copolymer composition is that shown in Table 3. This table also summarizes the weight-average molecular weight $\bar{M}_w$ obtained by SLS, the number-average molecular weight $\bar{M}_n$, the polydispersity indexes determined by SEC, and intrinsic viscosity data $[\eta]$ in ethanol for all the copolymers under study. Fractions can be considered as relatively monodisperse. From the data in Table 3 the Mark−Houwink−Kuhn−Sakurada (MHKS) relationships were established through log−log plots of $[\eta]$ vs $\bar{M}_w$. Straight lines with good correlations are obtained and the K_a and a parameters for each copolymer are collected in Table 4. Figures 3 and 4 show the MHKS plots for several copolymers containing MI and DI units, respectively, at the nearest 50% composition as examples of this kind of representation. The correlation R^2 for all the straight lines are also summarized in Table 4. From these plots, the K_a and a constants are obtained. These parameters show a normal behavior in the sense that K_a increases as a decreases. The values of the a exponent follows two different trends if the copolymer has MI or DI units. For copolymers containing MI units, in general a decreases as copolymer composition, expressed in terms of VP, increases; i.e., the solvent power, measured through the a values, diminishes as the VP content increases. A similar behavior is observed for the majority of the copolymers containing MI units, which is an unexpected result if we take into account that ethanol is a good solvent for the parent homopolymers.[30] Ex-

Table 3. Intrinsic Viscosity [η] in Ethanol at 298 K for Copolymers of MI−VP and DI−VP, Weight-Average Molecular Weight ($\bar{M}_w$), Number-Average Molecular Weight ($\bar{M}_n$) Obtained from the Polydispersity Index, and Polydispersity Indexes ($\bar{M}_w/\bar{M}_n$) for Various Fractions of Each Copolymer Determined by SEC

compstn (% VP)	fractn	[η]	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$	compstn (% VP)	fractn	[η]	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$
			MMI−VP						MEI−VP		
17	F_1	1.38	7.25	5.37	1.35	16	F_1	0.87	3.98	3.06	1.30
	F_2	1.03	4.50	3.46	1.30		F_2	0.78	2.92	2.24	1.30
	F_3	0.67	2.90	2.27	1.28		F_3	0.44	1.17	0.91	1.29
	F_4	0.48	1.91	1.47	1.30		F_4	0.25	0.60	0.48	1.26
	F_5	0.38	1.16	0.93	1.25		F_5	0.21	0.48[a]	0.40	1.20
	F_6	0.28	0.89[a]	0.75	1.19		F_6	0.12	0.25[a]	0.20	1.22
	F_7	0.16	0.46[a]	0.35	1.30	51	F_1	0.51	1.84	1.47	1.25
48	F_1	0.91	5.10	4.25	1.20		F_2	0.37	1.41	1.10	1.28
	F_2	0.52	2.40	2.03	1.18		F_3	0.21	0.61	0.48	1.28
	F_3	0.46	1.74	1.29	1.35		F_4	0.18	0.48	0.37	1.30
	F_4	0.29	0.99	0.78	1.27		F_5	0.18	0.40	0.31	1.30
	F_5	0.21	0.59[a]	0.46	1.27		F_6	0.15	0.31[a]	0.23	1.35
79	F_1	0.83	5.50	4.40	1.25	84	F_1	0.50	2.70	2.00	1.37
	F_2	0.63	2.85	2.47	1.15		F_2	0.24	0.83	0.64	1.30
	F_3	0.40	1.91	1.45	1.30		F_3	0.19	0.51	0.39	1.33
	F_4	0.33	1.41	1.07	1.32		F_4	0.17	0.43	0.33	1.30
	F_5	0.27	0.90[a]	0.70	1.28		F_5	0.13	0.30[a]	0.23	1.29
	F_6	0.19	0.55[a]	0.41	1.35						
			MPI−NP						MAI−VP		
18	F_1	0.91	4.27	6.53	1.20	26	F_1	0.36	2.14	1.64	1.30
	F_2	0.54	2.31	4.80	1.22		F_2	0.26	1.15	0.90	1.28
	F_3	0.43	1.78	4.22	1.25		F_3	0.19	0.65	0.49	1.33
	F_4	0.25	0.70	2.65	1.25		F_4	0.14	0.32[a]	0.24	1.34
	F_5	0.19	0.48	2.19	1.30		F_5	0.12	0.23[a]	0.17	1.35
	F_6	0.18	0.39	1.97	1.30	56	F_1	0.46	3.72	3.10	1.20
	F_7	0.12	0.25[a]	1.58	1.35		F_2	0.36	2.63	2.10	1.25
45	F_1	0.64	3.20	5.66	1.29		F_3	0.23	1.07	0.82	1.30
	F_2	0.33	1.20	3.46	1.28		F_4	0.19	0.74	0.58	1.28
	F_3	0.27	0.86	2.93	1.30		F_5	0.15	0.48[a]	0.40	1.20
	F_4	0.19	0.53	2.30	1.35	77	F_1	0.41	3.47	2.84	1.22
	F_5	0.13	0.27[a]	1.64	1.30		F_2	0.32	2.11	1.72	1.23
72	F_1	0.87	5.60	7.48	1.30		F_3	0.21	1.08	0.83	1.30
	F_2	0.39	1.70	4.12	1.29		F_4	0.17	0.68	0.52	1.31
	F_3	0.28	0.97	3.11	1.32		F_5	0.13	0.44	0.36	1.22
	F_4	0.25	0.78	2.79	1.35		F_6	0.12	0.36[a]	0.29	1.22
	F_5	0.16	0.41[a]	2.02	1.38						
	F_6	0.11	0.21[a]	1.45	1.40						
			DMI−VP						DEI−VP		
22	F_1	1.11	1.72	1.32	1.30	31	F_1	0.58	1.12	0.94	1.20
	F_2	0.85	1.02	0.78	1.32		F_2	0.36	0.66	0.53	1.25
	F_3	0.72	0.79	0.59	1.35		F_3	0.27	0.44	0.34	1.30
	F_4	0.62	0.62	0.47	1.30		F_4	0.28	0.33[a]	0.26	1.30
	F_5	0.41	0.28	0.21	1.30		F_5	0.21	0.24[a]	0.18_5	1.30
	F_6	0.34	0.21[a]	0.17	1.28	60	F_1	0.87	3.02	2.24	1.35
62	F_1	1.20	2.18	1.62	1.35		F_2	0.60	1.68	1.29	1.30
	F_2	0.60	0.68	0.53	1.28		F_3	0.42	0.94	0.73	1.30
	F_3	0.49	0.43	0.33	1.30		F_4	0.35	0.74	0.62	1.20
	F_4	0.38	0.28	0.22	1.25		F_5	0.26	0.50	0.40	1.25
	F_5	0.32	0.23[a]	0.18	1.30		F_6	0.20	0.27[a]	0.20	1.35
88	F_1	1.04	2.40	1.85	1.30	89	F_1	0.72	2.60	1.97	1.32
	F_2	0.49	0.83	0.67	1.25		F_2	0.44	1.19	0.93	1.28
	F_3	0.43	0.65	0.54	1.22		F_3	0.32	0.78	0.62	1.25
	F_4	0.33	0.43	0.33	1.28		F_4	0.23	0.42	0.32	1.30
	F_5	0.28	0.31[a]	0.23	1.30		F_5	0.15	0.25[a]	0.18	1.35
			DPI−VP						DAI−VP		
30	F_1	1.20	5.37	3.84	1.40	28	F_1	0.75	2.75	2.12	1.30
	F_2	0.80	2.19	1.62	1.35		F_2	0.62	2.04	1.63	1.25
	F_3	0.60	1.45	1.07	1.36		F_3	0.51	1.27	1.02	1.25
	F_4	0.46	0.91	0.67	1.35		F_4	0.26	0.35	0.28	1.24
	F_5	0.42	0.74	0.57	1.31		F_5	0.21	0.26[a]	0.21	1.23
	F_6	0.28	0.32	0.24	1.35	57	F_1	0.51	1.82	1.41	1.29
	F_7	0.23	0.24[a]	0.18	1.30		F_2	0.39	1.07	0.86	1.25
54	F_1	0.60	1.68	1.40	1.20		F_3	0.27	0.52	0.42	1.24
	F_2	0.54	1.35	1.11	1.22		F_4	0.24	0.40	0.32	1.25
	F_3	0.40	0.72	0.58	1.25		F_5	0.21	0.29[a]	0.23	1.25
	F_4	0.37	0.69	0.53	1.30	88	F_1	0.48	2.07	1.59	1.30
	F_5	0.27	0.38	0.29	1.29		F_2	0.39	1.45	1.11	1.30
	F_6	0.21_5	0.25[a]	0.20	1.20		F_3	0.26	0.66	0.52	1.28
82	F_1	0.64_5	2.63	1.95	1.35		F_4	0.21	0.39	0.32	1.20
	F_2	0.47	1.45	1.11	1.30		F_5	0.20	0.30	0.23	1.30
	F_3	0.34	0.81	0.62	1.32						
	F_4	0.28_5	0.58	0.45	1.29						
	F_5	0.24	0.42	0.32	1.30						

[a] Obtained by SEC.

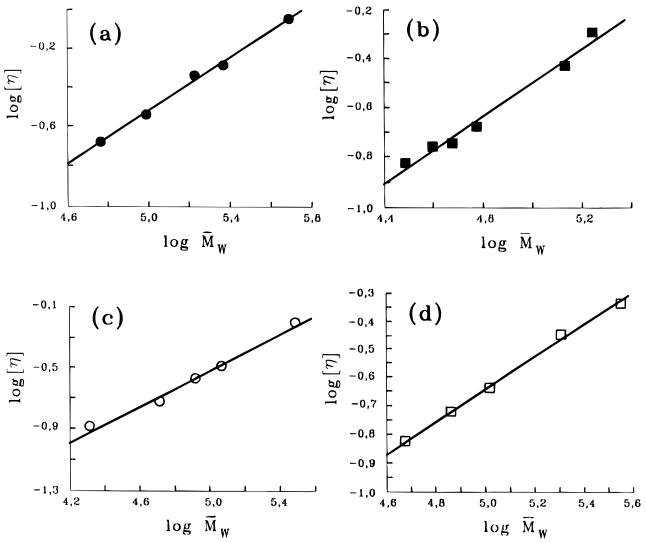

Figure 3. log−log plots of intrinsic viscosity [η] and weight-average molecular weight $\bar{M}_w$ for MI-*co*-VP copolymers of ∼50% composition: (a) MMI-*co*-VP; (b) MEI-*co*-VP; (c) MPI-*co*-VP; (d) MAI-*co*-VP.

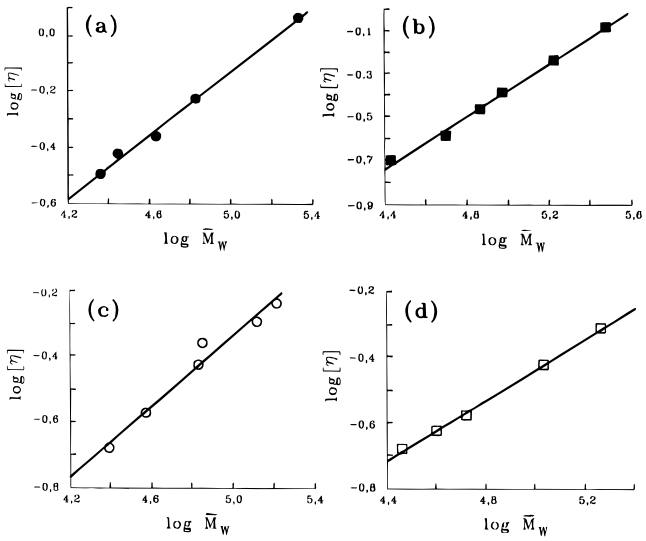

Figure 4. log−log plots of intrinsic viscosity [η] and weight-average molecular weight $\bar{M}_w$ for DI-*co*-VP copolymers of ∼50% composition: (a) DMI-*co*-VP; (b) DEI-*co*-VP; (c) DPI-*co*-VP; (d) DAI-*co*-VP.

ception to this behavior arise for MAI−VP copolymers. In the same group of copolymers, those with similar compositions but different structure show that the *a* value decreases as the length of the side chain of the monoitaconate unit increases. On the other hand, for copolymers containing DI units, a general decrease of the solvent power of ethanol is found, relative to copolymers containing monoitaconates, and the *a* values observed are very close. These results could be interpreted in terms of an effect of the side-chain structure on the thermodynamic behavior of the copolymers. In the case of copolymers containing diitaconate units, the free carboxylic group is replaced by an alkyl group which could influence the solubility and the thermodynamic behavior in solution of these polymers. In the case of copolymers containing DI units, there is an increment of the steric hindrance in the monomer unit which can also be another factor to take into account for the explanation of the solubility and thermodynamic behavior. Perhaps the effect of the comonomer sequence in these copolymers should be analyzed, considering

Table 4. MHKS Parameters for the Various Copolymers of MI−VP and DII−VP, Conformational Parameter K_Θ, and Long-Range Interaction Parameter *B*, Obtained from the Stockmayer−Fixman Equation

copolymer	compstn (% VP)	$K_a \times 10^4$	*a*	R^2	$K_\Theta \times 10^{2\,a}$	$B \times 10^{28\,b}$	R^2
MMI−VP	17	0.42	0.77	0.983	5.4	10.5	0.724
	48	1.20	0.68	0.996	6.8	6.6	0.929
	79	1.35	0.66	0.994	6.8	5.4	0.937
MEI−VP	16	0.81	0.72	0.997	6.4	11.5	0.893
	51	1.51	0.67	0.981	5.9	9.7	0.837
	84	2.76	0.60	0.991	6.9	4.0	0.911
MPI−VP	18	1.35	0.68	0.990	6.2	8.7	0.966
	45	3.62	0.59	0.987	6.5	6.7	0.986
	72	1.23	0.67	0.994	6.7	5.2	0.943
MAI−VP	26	7.78	0.50	0.984	7.1	0.0	0.963
	56	3.49	0.56	0.996	6.5	1.2	0.880
	77	3.24	0.56	0.998	6.0	1.3	0.970
DMI−VP	22	12.90	0.56	0.991	21.7	11.1	0.984
	62	9.61	0.58	0.995	20.2	9.3	0.964
	88	4.24	0.63	0.979	12.4	13.9	0.942
DEI−VP	31	7.68	0.57	0.992	10.2	15.6	0.932
	60	3.07	0.63	0.994	10.2	8.1	0.958
	89	1.92	0.66	0.624	8.1	9.4	0.880
DPI−VP	30	12.60	0.52	0.869	14.9	1.7	0.973
	54	8.90	0.54	0.974	13.2	2.2	0.936
	82	9.80	0.52	0.980	11.1	2.3	0.908
DAI−VP	28	9.82	0.53	0.989	13.3	1.3	0.823
	57	11.95	0.50	0.998	11.5	0.0	0.959
	88	10.55	0.50	0.924	9.7	0.0	0.997

[a] In $cm^3\ g^{-3/2}\ mol^{-1}$. [b] In $cm^3\ mol^{-2}\ g^{-2}$.

that they exhibit high reactivity ratios and perhaps a tendency to block formation. Therefore, the effect of the solution behavior of the comonomer VP inserted on the poly(itaconate) chains seems to be reflected in the *a* values when these data are compared with those of the corresponding parent homopolymers.

The unperturbed root mean square end-to-end dimension $(\langle r^2\rangle_o/M)^{1/2}$ for the different copolymers was obtained using the classical relationship

$$K_\Theta = \Phi_o(\langle r^2\rangle_o/M)^{1/2} \tag{7}$$

where Φ_o is the universal Flory[31] constant; the best value is 2.51×10^{21} (cgs). K_Θ is determined using the Stockmayer−Fixman (SF)[32] equation:

$$[\eta]/M^{1/2} = K_\Theta + 0.51\Phi_o B\bar{M}_w^{1/2} \tag{8}$$

where *B* is the long-range interaction parameter related to the excluded-volume parameter. In order to obtain the chain rigidity factor defined as

$$\sigma = (\langle r^2\rangle_o/\langle r^2\rangle_{of})^{1/2} \tag{9}$$

the root mean square end-to-end distance for a completely free rotation around the bonds $(\langle r^2\rangle_{of}/M)^{1/2}$ can be determined for the copolymers, taking into account the copolymer composition, when the molecular weight of the monomer unit of the corresponding copolymer is considered.[33] In fact, in the calculation of $(\langle r^2\rangle_{of}/M)^{1/2}$ for homopolymers, the molecular weight of the monomer unit must be considered, therefore, in the case of copolymers, this magnitude should be pondered according to the copolymer composition, which is one of the approximations in this kind of calculations. SF plots for all the systems studied for various compositions show in all cases straight lines, which correlations are summarized in Table 4. The K_Θ and *B* values determined from the intercept and slope of the SF plots are

Table 5. Root Mean Square End-to-End Distance ($\langle r^2\rangle_{of}/M)^{1/2}$, Unperturbed Chain Dimensions ($\langle r^2\rangle_o/M)^{1/2}$ Rigidity Factor σ, and Characteristic Ratio C_∞ for MI−VP and DI−VP Copolymers

polym/ copolym	compstn (mol % [VP])	$(\langle r^2\rangle_o/M)^{1/2}$	$(\langle r^2\rangle_{of}/M)^{1/2}$	σ	C_∞	ref
PMMI	0.0	0.582	0.257	2.28	10.6	30a
MMI−VP	17	0.724	0.262	2.76	10.3	*a*
	48	0.659	0.272	2.42	11.1	*a*
	79	0.659	0.283	2.32	10.2	*a*
PMEI	0.0	0.620	0.245	2.53	12.9	30b
MEI−VP	16	0.646	0.251	2.57	12.5	*a*
	51	0.628	0.266	2.36	10.6	*a*
	84	0.662	0.283	2.34	10.4	*a*
PMPI	0.0	0.615	0.234	2.62	12.9	*b*
MPI−VP	18	0.639	0.243	2.63	13.1	*a*
	45	0.649	0.256	2.54	9.6	*a*
	72	0.656	0.272	2.41	11.0	*a*
PMAI	0.0	0.632	0.218	2.90	16.0	*b*
MAI−VP	26	0.669	0.231	2.89	15.8	*a*
	56	0.649	0.251	2.59	12.6	*a*
	77	0.632	0.269	2.35	10.5	*a*
PDMI	0.0	0.494	0.245	2.02	7.9	5
DMI−VP	22	0.970	0.253	3.83	27.7	*a*
	62	0.947	0.271	3.49	25.9	*a*
	88	0.805	0.285	2.82	15.1	*a*
PDEI	0.0	0.447	0.226	1.98	7.7	5
DEI−VP	31	0.754	0.328	2.29	18.5	*a*
	60	0.754	0.259	2.91	12.7	*a*
	89	0.698	0.282	2.48	11.6	*a*
PDPI	0.0	0.478	0.211	2.27	10.1	5
DPI−VP	30	0.856	0.228	3.75	26.8	*a*
	54	0.822	0.245	3.36	21.4	*a*
	82	0.763	0.271	2.82	15.6	*a*
PDAI	0.0	0.529	0.187	2.82	15.1	*b*
DAI−VP	28	0.824	0.205	>4.0	25.6	*a*
	57	0.785	0.230	3.41	20.1	*a*
	88	0.729	0.270	2.70	14.6	*a*
PVP	100	0.650	0.290	2.24	8.7	11, 30c

[a] This work. [b] Estimated values by interpolation with closely related polymers.

also summarized in Table 4. According to these results, K_Θ values for the various copolymers depend on the copolymer composition. Comparison of the K_Θ values for copolymers containing MI and DI units shows important differences, in fact, the K_Θ values in the former family are lower than those for diitaconate copolymers. This effect can be analyzed through the rigidity index σ for each copolymer as defined by eq 9. Nevertheless the most used and appropriate value for comparison of the steric hindrance to rotation in a polymeric chain is the characteristic ratio C_∞ as defined by Flory:[31]

$$C_\infty = \lim_{n\to\infty}\left[\frac{\langle r^2\rangle_o}{nl^2}\right] \qquad (10)$$

with n the number of main-chain bonds of mean square length l^2. Table 5 compiles the values for the root mean square end-to-end distance for a completely free rotation chain model $(\langle r^2\rangle_{of}/M)^{1/2}$, the unperturbed dimensions $(\langle r^2\rangle_o/M)^{1/2}$, the rigidity factor σ, and the characteristic ratio C_∞ determined for all copolymers of varying compositions and for corresponding parent homopolymers taken from literature.

Table 6. Glass Transition Temperature (T_g) for Copolymers of VP-*co*-MI and VP-*co*-DI at Different Compositions

polymers	compstn (mol % [VP])	Tg/°C	ref
PMMI		∼150[a]	37
MMI−VP	17	142	*b*
	48	140	*b*
	79	142	*b*
PMEI		∼130	37
MEI−VP	16	127	*b*
	51	125	*b*
	84	135	*b*
PMPI		∼120[a]	37
MPI−VP	18	111	*b*
	45	115	*b*
	72	124	*b*
PMAI		98[a]	37
MAI−VP	26	96	*b*
	56	105	*b*
	77	110	*b*
PDMI		99	38
DMI−VP	22	130	*b*
	62	139	*b*
	88	145	*b*
PDEI		52	38
DEI−VP	31	98	*b*
	60	121	*b*
	89	141	*b*
PDPI		25	38
DPI−VP	30	86	*b*
	54	106	*b*
	82	136	*b*
PDAI		20	38
DAI−VP	28	68	*b*
	57	103	*b*
	88	138	*b*

[a] Obtained by extrapolation in blends.[37] [b] This work.

The results shown in Table 5 indicate that conformational parameters for the first family of copolymers, i.e., those containing monoitaconate units, are rather similar to that of the corresponding homopolymer. However, for copolymers with diitaconate units, there is an important increment of the conformational parameters. Both families of copolymers behave in different ways. This behavior could be explained by taking into account that vinylpyrroline readily undergoes inter- and intramolecular association, through, e.g., hydrogen bonding and/or dipole−dipole interaction.[19] On the other hand, in the case of MI−VP, copolymers could be a kind of balance between the interactions due to the carboxyl and VP groups.

It is well documented that changes in the conformational characteristics of PVP, produced by interactions that are sensitive to dielectric constant and molecular size of the solvent, may be responsible, at least in part, for the differences in the dimensions of the chains obtained by evaluation of viscosity measurements in different solvents.[34] Therefore, the conformational behavior of these copolymers should be strongly affected by the solvent interaction and the comonomeric mutual interaction.

In previous work[1] it was reported that poly(mono-*n*-alkyl itaconates) with long alkyl side chains, e.g., decyl and dodecyl groups, behave as stiff polymers and their solution properties can be described using a wormlike

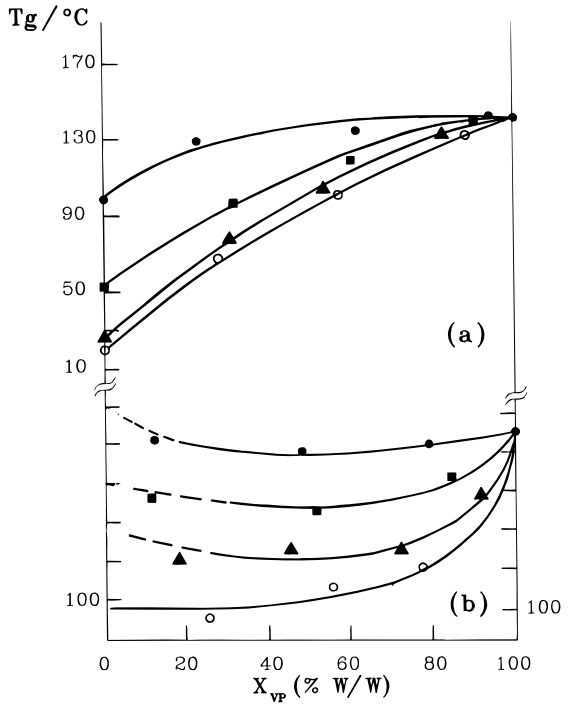

Figure 5. Dependence of the glass transition temperature T_g on composition. (a) DI-*co*-VP copolymers: (●) DMI-*co*-VP; (■) DEI-*co*-VP; (▲) DPI-*co*-VP; (○) DAI-*co*-VP. (b) MI-*co*-VP copolymers: (●) MMI-*co*-VP; (■) MEI-*co*-VP; (▲) MPI-*co*-VP, (○) MAI-*co*-VP.

model.[1a,b] On the other hand, when these monoalkyl itaconates are copolymerized with vinylpyrrolidone, the stiffness of the polymer chain diminishes.[11a] Therefore, the solution behavior of the copolymers could be analyzed in terms of linear flexible coils.[11a] On the other hand, the first members of the series of poly(monoitaconates) behave as linear flexible coils with reasonable values for the rigidity factor and characteristic ratios as shown in Table 5 taken from the literature.[30a,b]

Similar behavior is observed for poly(diitaconates) with short side chains[35] in the sense that these polymers present conformational parameters that can be considered as flexible chain molecules. The increment of the characteristic ratio C_∞ can be explained in terms of an enhancement of the specific interaction due to the presence of VP units, as was explained above. These results are in good agreement with those obtained for the reactivity ratios, the thermodynamic parameters, and also the T_g values shown in Figure 5.

It is very well known that blends containing poly(monoitaconates) and poly(vinylpyrrolidone) readily undergoes interpolymer complexes (IC) formation in solution as well as in the solid state.[36] This phenomenon has been attributed to different kind of specific interactions,[26c,d,37] mainly to hydrogen bond formation through the free carboxylic group of the poly(monoitaconate), but in poly(diitaconates) this possibility is unfavorable. When interpolymer complex formation takes place, it can be considered a special kind of association and packing of the polymers, and therefore, the glass transition temperature, T_g, shows significant variations relative to the pure polymers.[36] However, copolymers containing the same monomeric units as that of the pure homopolymers may not necessarily behave in a similar way. Nevertheless, in the case of VP-*co*-DI copolymers, it could be interpreted there is a behavior similar to that of IC. Table 6 shows the values of the T_g for the different copolymers, and Figure 5 represents the variation of T_g with composition. The values of T_g's of poly(monoitaconate) homopolymers were estimated by T_g extrapolation of blends[38] containing these polymers, and T_g values for poly(diitaconates) were obtained from the literature.[39] It is important to take into account that the T_g values for the hompolymers are not $T_{g\infty}$. As can be seen in Table 6 the T_g values for copolymers containing DI units follow a different trend from those containing MI units. VP-*co*-MI copolymers show a monotonic variation of T_g with composition below the ponderated average between the corresponding homopolymers. In the case of VP-*co*-DI, there is an enhancement of the T_g values over the ponderated average between the homopolymers.

These results should be correlated with those obtained in solution, and the enhancement of the polymer rigidity in VP-*co*-DI copolymers could be explained in this way. On the other hand, as was discussed above, from the results of the reactivity ratios, the copolymer structure seems to be quite different if MI or DI units are present. Thus, the apparent anomalous behavior of DI-*co*-VP copolymer could be understood as an effect of the polymer structure, due mainly to the monomer distribution. It is difficult to understand this peculiar behavior. Nevertheless, it is necessary to take into account that comparison between structures containing mono- and diitaconates should be carefully analyzed due to the different nature of the interactions involved in both systems.

Further investigations dealing with the effect of the side chain structure on the conformational behavior of copolymers are in progress.

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