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N-1-ALKYLITACONAMIC ACIDS-CO-STYRENE COPOLYMERS. 1. SYNTHESIS, CHARACTERIZATION AND MONOMER REACTIVITY RATIOS

M. Urzúa^a; N. Gatica^a; L. Gargallo^a; D. Radić

^a Depto. Química Física Facultad de Química, Pontificia Universidad Católica de Chile, Santiago 22, Chile

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M. Urzúa, N. Gatica, L. Gargallo, and D. Radic^{**}

Depto. Química Física
Facultad de Química
Pontificia Universidad Católica de Chile
Casilla 306, Santiago 22, Chile

ABSTRACT

Copolymers containing N-1-ethylitaconamic acid, N-1-propylitaconamic acid, N-1-butylitaconamic acid, N-1-hexylitaconamic acid, N-1-octylitaconamic acid and N-1-decylitaconamic acid with styrene of different comonomer compositions were synthesized and characterized. Copolymer composition was determined by elemental analysis following the nitrogen content in the resulting copolymers. Monomer reactivity ratios r_1 and r_2 of the different copolymers were estimated using straight line intersection procedures such as Fineman-Ross (F-R) and Kelen-Tüdös (K-T) and by a nonlinear one, according to the reactivity ratios error-in-variables model (RREVM). Good agreement between the different procedures for r_1 and r_2 determination was found. Differences in the reactivity of N-1-alkylitaconamic acids (NAIA) relative to styrene were found i.e., ethyl and propyl derivative are less reactive with itself than butyl, hexyl, octyl,

^{*}Author to whom correspondence should be addressed.

Fax: 56-2-6864744, E-mail: dradic@puc.cl

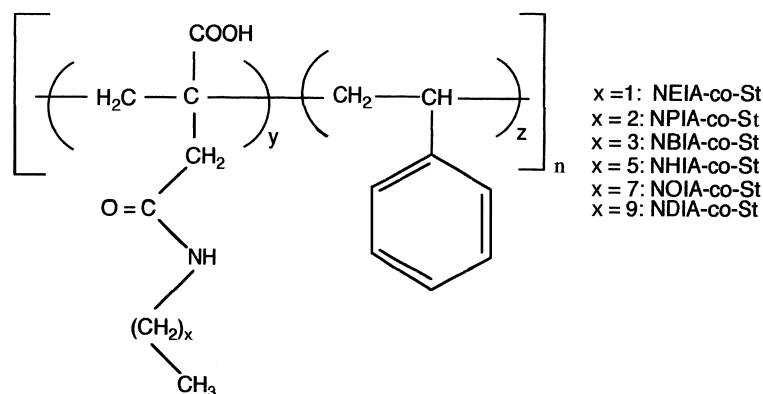
and decyl derivatives with itself. Copolymers with some tendency toward small block formation are found.

INTRODUCTION

Increasing attention is currently being directed to the synthesis of copolymers containing both hydrophilic and hydrophobic segments, i.e., amphiphilic polymers [1]. Copolymers with variable amounts of both types of structures can be considered as good models for interactions in biological systems, mainly because of the possibility to produce a chemically homologous series of surfaces varying principally in hydrophilicity [2].

Functionalization of polymers and copolymers is a suitable way to obtain amphiphilic interacting polymer systems [3]. Copolymers containing itaconate units are of interest due to their interacting nature and to the variety of structures that are possible to be obtained. Particularly interesting are mono-*n*-alkyl-itaconates as comonomers because they have the capacity to interact via hydrogen bonding through the free carboxylic groups [4, 5]. On the other hand, poly(itaconamic) acids are a family of polymers derived from itaconic acid which can be classified as strongly interacting amphiphilic polymers [6, 7]. In fact, these polymers contain a free carboxylic and amide group per monomer unit, which should be able to interact specifically by hydrogen bonding formation with different acceptor polymers; this is of interest in the study of polymer-polymer miscibility. The alkyl side chain in these polymers can be varied, resulting in polymers with different side chain length, thus controlling the hydrophobicity [6, 7]. Therefore, it should be expected that a balance between the length of the alkyl side chain and the free carboxylic group would allow us to obtain a specific amphiphilic molecule. Copolymerization of these molecules with another hydrophobic or hydrophilic comonomer should give macromolecules with a good controlled chemical architecture. However, to reach this objective it is necessary to know accurately the monomer reactivity ratios and therefore, the comonomer sequence.

The aim of the present work was the synthesis, characterization, and determination of the monomer reactivity ratios (MRR) of *N*-1-alkylitaconamic acids-co-styrene copolymers (NAIA-co-St) (See Scheme 1). In order to study the effect of changing the nature and length of the side chain in this kind of systems, copolymers containing ethyl (NEIA), 1-propyl (NPIA), 1-butyl (NBIA), 1-hexyl (NHIA), 1-octyl (NOIA) and 1-decyl, (NDIA) groups were studied.



Scheme 1.

EXPERIMENTAL

Monomers and Polymer Preparation

N-1-alkylitaconamic acids (NAIA) were synthesized by the reaction of itaconic anhydride with the corresponding 1-alkylamine in chloroform following procedures previously reported [6, 7] and improved by us. A sample of styrene from Merck, previously distilled under vacuum, was used for copolymerization. Copolymerization of the monomers was carried out in bulk at 354-388 K (depending on the N-1-alkylitaconamic acid used) under nitrogen using α , α' -azobisisobutyronitrile (AIBN) (0.6 mol%) as initiator. The conversions of most of the copolymers were rather low (<10%). Purification of the copolymers was achieved by reprecipitation with methanol in a THF solution before vacuum drying.

Copolymer Characterization

Copolymers were characterized by $^1\text{H-NMR}$ in a Bruker AC-200 spectrometer using TMS as an internal standard and deuterium oxide as a solvent. F.T.I.R. spectra were recorded on a Vector 22 Bruker Fourier transform infrared spectrophotometer. The spectra were recorded with a resolution of 1 cm^{-1} . The samples were prepared directly in KBr pellets. Composition of the copolymers were determined by elementary analysis measurements following the nitrogen content in the copolymer.

RESULTS AND DISCUSSION

The monomer molar composition in the feed (M_1 and M_2) and the resulting monomer molar composition in the copolymer dM_1 and dM_2 (styrene = monomer 1) are compiled in Table 1.

TABLE 1. Copolymerization data for NEIA-co-St, NPJA-co-St, NBIA-co-St, NHIA-co-St, NOIA-co-St and NDIA-co-St copolymers: composition in feed (M_1) resulting composition (dM_1), X, Y, F, and G, as defined by Fineman-Ross (F-R) [9], ξ , η and α parameters as defined by Kelen- Tüdös (K-T) [10].

Copolymer	M_1	dM_1	X	Y	F	G	η	ξ
	mol %	mol%						
NEIA-co-St ^a	20	30.17	0.250	0.432	0.144	-0.328	-0.379	0.167
	40	67.59	0.667	2.085	0.215	0.349	0.373	0.229
	50	72.64	1.000	2.655	0.623	0.376	0.279	0.463
	60	75.39	1.500	3.063	0.734	1.010	0.694	0.504
	80	81.67	4.000	4.455	3.591	3.100	0.719	0.832
NPJA-co-St ^b	20	33.34	0.250	0.500	0.125	-0.249	-0.353	0.176
	40	43.48	0.667	0.769	0.468	-0.180	-0.171	0.445
	50	58.27	1.000	1.396	0.716	0.248	0.218	0.551
	60	72.26	1.500	2.605	0.864	0.924	0.638	0.597
	80	85.43	4.000	5.863	2.729	3.318	1.002	0.824
NBIA-co-St ^c	20	14.68	0.250	0.172	0.363	-1.203	-0.597	0.180
	40	36.07	0.667	0.564	0.788	-0.515	-0.327	0.500
	50	46.45	1.000	0.867	1.153	-0.153	0.055	0.411
	60	48.70	1.500	0.949	2.370	-0.080	0.020	0.589
	80	68.02	4.000	2.127	7.523	2.119	0.231	0.820
NHIA-co-St ^d	20	15.39	0.250	0.183	0.344	-1.123	-0.677	0.207
	40	30.77	0.667	0.444	1.002	-0.835	-0.393	0.471
	50	48.99	1.000	0.960	1.041	-0.041	-0.017	0.041
	60	50.38	1.500	1.015	2.216	0.023	0.006	0.627
	80	76.07	4.000	3.179	5.033	2.742	0.432	0.792
NOIA-co-St ^e	20	7.92	0.250	0.086	0.726	-2.656	-1.056	0.288
	40	35.32	0.667	0.546	0.814	-0.554	-0.212	0.312
	50	44.53	1.000	0.802	1.246	-0.246	-0.081	0.410
	60	55.08	1.500	1.226	1.835	0.276	0.076	0.506
	80	78.42	4.000	3.634	4.402	2.899	0.468	0.711
NDIA-co-St ^f	20	10.12	0.250	0.112	0.558	-1.982	-0.903	0.254
	40	40.05	0.667	0.668	0.672	-0.331	-0.143	0.291
	50	54.65	1.000	1.205	0.829	0.170	0.068	0.336
	60	67.21	1.500	2.049	1.098	0.768	0.208	0.297
	80	76.94	4.000	3.336	4.796	2.801	0.563	0.964

a. monomer 1= St, 2 = NEIA, $\alpha = 0.720$

b. monomer 1= St, 2 = NPJA, $\alpha = 0.584$

c. monomer 1= St, 2 = NBIA, $\alpha = 1.652$

d. monomer 1= St, 2 = NHIA, $\alpha = 1.316$

e. monomer 1= St, 2 = NOIA, $\alpha = 1.787$

f. monomer 1= St, 2 = NDIA, $\alpha = 1.636$

In order to characterize the copolymer sequences, the monomer reactivity ratios (MRR) r_1 and r_2 were determined following a mathematical procedure previously reported [3, 8]. The least squares method according to Fineman and Ross [9] (FR) was used by plotting G against F according to Equations 1 and 2.

$$G = Fr_1 - r_2 \quad (1)$$

with

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

where $x = \frac{M_1}{M_2}$ and $y = \frac{dM_1}{dM_2}$

Monomer reactivity ratios (MRR) r_1 and r_2 were also determined by the Kelen-Tüdös treatment [10] (KT method), according to Equation 3:

$$\eta = \left(r_1 + \frac{r_2}{\alpha} \right) \xi - \frac{r_2}{\alpha} \quad (3)$$

where η and ξ are mathematical functions of mol composition ratios of monomers in feed and in the copolymer, defined as:

$$\eta = \frac{G}{\alpha + F} \quad \text{and} \quad \xi = \frac{F}{\alpha + F} \quad (4)$$

with a an arbitrary constant, defined as: $\alpha = (F_l F_h)^{\overline{2}}$ where F_l and F_h are the lowest and highest values of F , respectively. According to these equations, plots of the η values calculated from experimental data as a function of ξ , should be straight lines which, extrapolated to $\xi = 0$ and $\xi = 1$, allow determination of r_1 and r_2 (both as intercepts). The values of the different parameters determined by eqns. (1) and (3) are also summarized in Table 1. Figure 1 shows the Fineman-Ross [9] and Kelen-Tüdös [10] plots for NPAA-co-St, NBIA-co-St, and NHIA-co-St, respectively as representative examples of this kind of representation (plots corresponding to the other copolymers were not included for the sake of clarity). r_1 and r_2 values obtained from these plots are compiled in Table 2. Good agreement between both procedures for the determination of r_1 and r_2 is found in the sense that both follow the same trend. However, it is important to

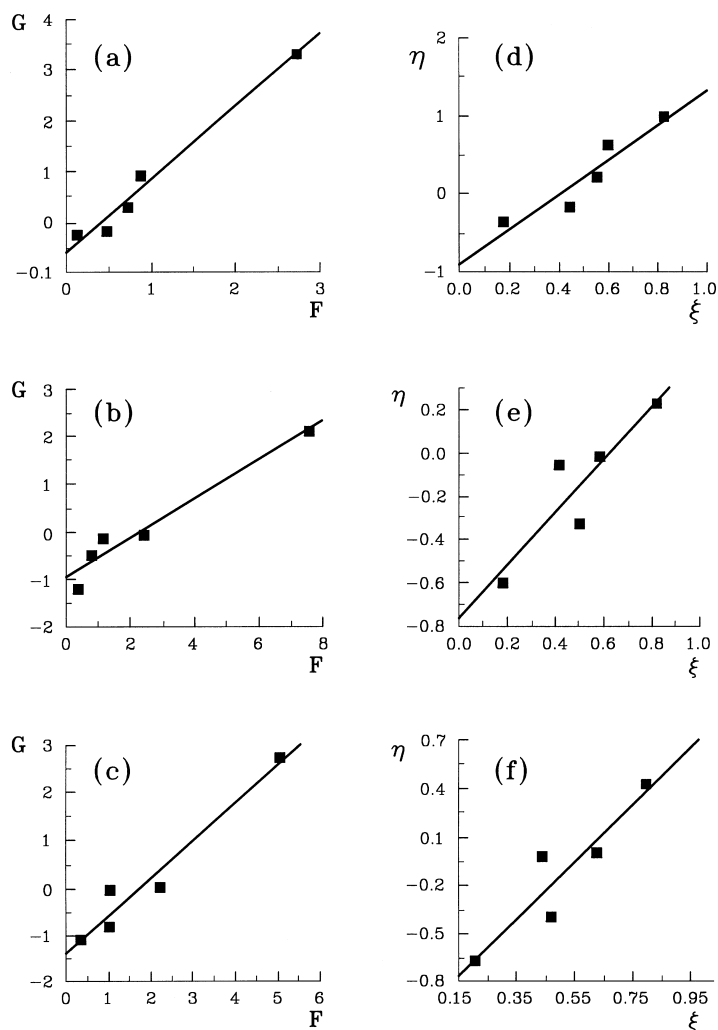


Figure 1. Fineman Ross representation of the copolymerization parameters for (a) NPIA-co-St, (b) NBIA-co-St, (c) NHIA-co-St copolymers and Kelen-Tüdös representation of the copolymerization parameters for (e) NPIA-co-St, (f) NBIA-co-St, (g) NHIA-co-St copolymers.

remark that due to the weakness of the linear methods, differences in the absolute values of r_1 and r_2 are observed; these should be attributed to the extent of the experimental error in the determination of the copolymer composition ($y = dM_1/dM_2$) and therefore, in the other parameters. The error in Figure 1 is a little bigger than the symbols used (2-3%). Nevertheless, these methods are powerful tools for the determination of MRR as a first approximation.

TABLE 2. Monomer Reactivity Ratios r_1 (St) and r_2 (NAIA) obtained by the Fineman-Ross (F-R) [9], Kelen-Tudos (K-T) [10] and Reactivity Ratio Error In Variable Method (RREVM) [11] methods for NEIA-co-St, NPIA-co-St, NBIA-co-St, NHIA-co-St, NOIA-co-St and NDIA-co-St copolymers.

Copolymer	Methods	r_1	r_2	$r_1 r_2$
NEIA-co-St	FR	1.57	0.38	0.59
	KT	1.06	0.16	0.17
	RREVM	1.15	0.35	0.40
NPIA-co-St	FR	1.43	0.59	0.84
	KT	1.34	0.52	0.69
	RREVM	1.02	0.34	0.35
NBIA-co-St	FR	0.41	0.98	0.40
	KT	0.45	1.26	0.57
	RREVM	0.74	1.43	1.05
NHIA-co-St	FR	0.80	1.39	1.11
	KT	0.75	1.37	1.03
	RREVM	0.76	1.43	1.09
NOIA-co-St	FR	0.98	1.44	1.41
	KT	0.95	1.38	1.31
	RREVM	0.84	1.31	1.10
NDIA-co-St	FR	0.83	1.03	0.85
	KT	0.66	0.93	0.61
	RREVM	1.44	1.60	2.30

monomer 1 = St, monomer 2 = NEIA, NPIA, NBIA, NHIA, NOIA or NDIA

In order to obtain more reliable values of MRR, they can also be estimated by using nonlinear methods based on the statistically valid error-in-variables model, (RREVM) or on its modifications [12-14]. These methods follow a nonlinear minimization algorithm (NLMA) using a computer program where no groups of variables are considered to be independent and free of error. As starting values, it is necessary to use the r_1 and r_2 obtained from the straight line iteration methods FR or KT. Figure 2 shows the 95% probability contours for r_1 and r_2 starting from the KT values taken from Table 2 for NEIA-co-St, NPIA-co-St, NBIA-co-St, NHIA-co-St, NOIA-co-St and NDIA-co-St copolymers using the RREVM program for the probability contour. In all cases, the r_1 and r_2 values obtained were generated using errors of 1% for the monomer feed

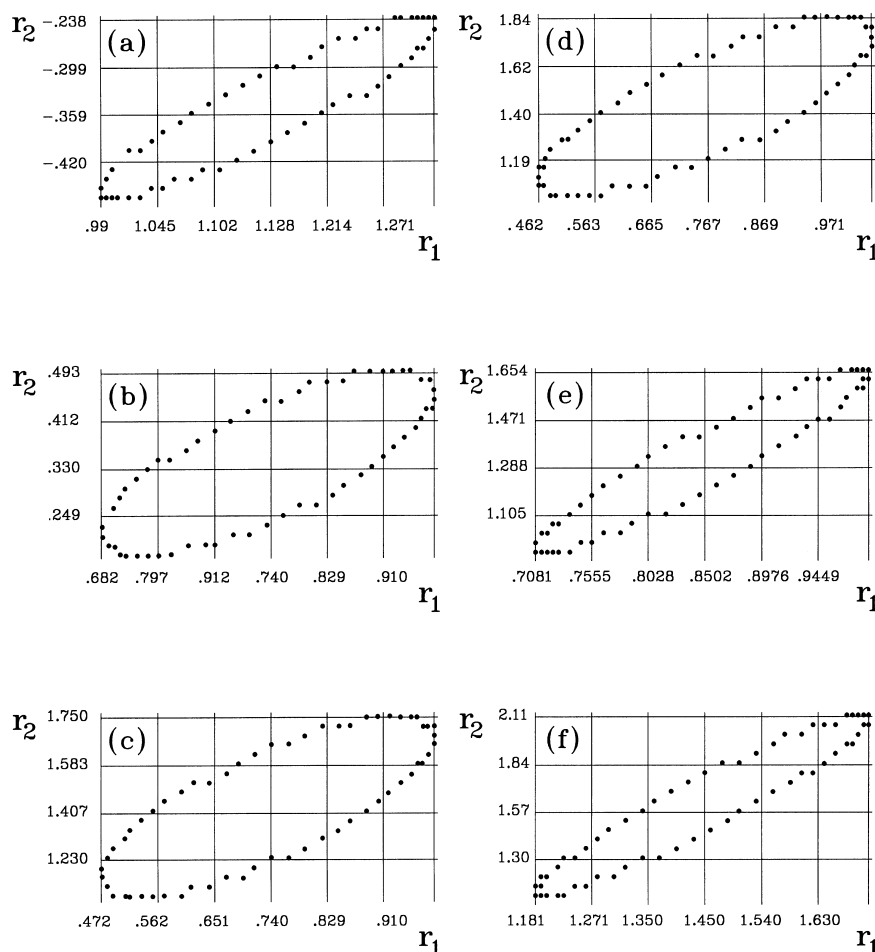


Figure 2. The 95% probability contour for estimated r_1 and r_2 values for (a) NEIA-co-St, (b) NPIA-co-St, (c) NBIA-co-St, (d) NHIA-co-St, (e) NOIA-co-St and (f) NDIA-co-St copolymers.

compositions and 2% for the copolymer composition. Mathematically, the algorithm minimizes the sum of squares of directed distances from the observed points to their estimated true values [11]. The values of r_1 and r_2 estimated by RREVM method for the copolymers studied are also compiled in Table 2. Comparison of the r_1 and r_2 values obtained by the three methods show differences, but the same trend in the sense that r_1 and r_2 values are higher or lower than unity.

When one of the monomer reactivity ratios is larger than unity, it means that one of the monomer is more reactive with itself than with the other comonomer. In this case, differences in the copolymer composition relative to the feed compositions are observed and therefore, more units of the most reactive comonomer will be inserted in the macromolecular chain. According to the data compiled in Table 2 for copolymers containing NEIA and NPJA, these comonomers are less reactive with themselves than with styrene. Therefore, these copolymers show some tendency toward the formation of blocks containing styrene. On the contrary, in the case of copolymers containing NBIA, NHIA, NOIA and NDIA there is an inversion of the reactivity ratios relative to the former systems. NBIA, NHIA, NOIA and NDIA show a larger affinity to react with themselves than with styrene. In this way, copolymers with some tendency toward the formation of small blocks of the corresponding NAIA is found. In the latter case, for NHIA and NOIA in particular, the values of r_1 and r_2 are larger than the unity and therefore, the tendency to block formation should be the dominant process. These results during radical copolymerization, can be explained in terms of steric hindrance and hydrophobic interaction in the copolymerization process. The relative monomer reactivity in radical copolymerization is conditioned by different factors such as polarity, steric hindrance and the stabilization by resonance of the propagating species. It is difficult to fully explain the results shown in this work. The results found for NEIA-co-St and NPJA-co-St are reasonable taking into account that the side chain doesn't affect the stabilization of the propagating species which are stabilized by the resonance in the aromatic ring. The resonance effect should be considered as constant for the five copolymers studied, because the amide group doesn't participate in the delocalization process by resonance, irrespective of the length of the side chain. However, the steric hindrance and polarity of the side chain could play an important role in the stabilization of the propagating radicals. As the length of the side chain increases, the hydrophobicity and steric hindrance increases. Therefore, the hydrophobic interaction together with the steric hindrance could affect the relative stabilization of the radical thus favoring the reactivity of NAIA with themselves rather than with styrene. By this way, it would be reasonable to think that in the stabilization process of the propagating species and therefore, on the relative monomer reactivities, a kind of balance between the three main factors take place. More important is the resonance effect when the aliphatic side chain is short; for long aliphatic side chains, the hydrophobic and steric effects are dominant. This behavior is qualitatively similar to that found for copolymers of styrene with n-alkylmethacrylates [14-17] i.e. hydrophobic effect on the reactiv-

ity ratios of the polymers. The correlation between the reactivity parameters and the structure of the side chain results in the increase in reactivity of NAIA with themselves with increasing side chain length, but NDIA decreases.

CONCLUSION

According to the results of monomer reactivity ratios obtained for copolymers containing NEIA, NPIA, NBIA, NHIA, NOIA, and NDIA with styrene, the copolymer sequence should have some tendency toward the formation of small blocks of styrene in the two former and of NBIA, NHIA, NOIA or NDIA in the four latter cases. Good agreement in the trend of r_1 and r_2 using the straight line intersection procedures and the nonlinear minimization algorithm is observed. The hydrophobic and steric effects seem to have an important role on the reactivity of the different monomers, controlling the monomer sequence of NAIA in the copolymer.

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