The Free-Radical Polymerization of Bicyclobutanes

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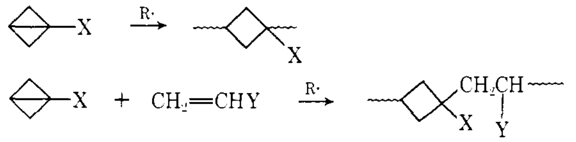
Abstract: Free-radical reactivity ratios were determined for the copolymerization of various bicyclobutanes possessing electronegative substituents at the bridgehead with typical vinyl monomers. The bicyclobutanes were as reactive as the vinyl compounds, a result ascribed to the high p character of the 1,3 bond. Homopolymerization of 1-bicyclobutanecarbonitrile in solution was controllable with isobutyraldehyde. Molecular weights were high (M_n = 45,000–85,000). Gel permeation chromatograms showed molecular weights skewed to the high side, owing to chain transfer with polymer followed by branching. In general, the bicyclobutanes behaved like vinyl monomers in free-radical polymerization.

The previous articles[2,3] of this series showed that bicyclobutanes carrying electronegative 1 substituents polymerize and copolymerize through a free-radical mechanism. The present paper presents reactivity ratios of these polymerizations, demonstration of chain transfer with isobutyraldehyde, and the molecular weights and distributions of the homopolymers of 1-bicyclobutanecarbonitrile.

Table I. Reactivity Ratios

B	V	Solvent	$r_B = \frac{k_{BB}}{k_{BV}}$	$r_V = \frac{k_{VV}}{k_{VB}}$	Comments
1-Bicyclobutane-carbonitrile	Styrene	DMSO	0.16	1.35	
1-Bicyclobutane-carbonitrile	Styrene	Methyl ethyl ketone	0.12	1.43	Heterogeneous
1-Bicyclobutane-carbonitrile	Styrene	γ-Butyrolactone	0.12	1.43	
1,3-Bicyclobutane-dicarbonitrile	Styrene	DMSO	0.01	1.09	
1,3-Bicyclobutane-dicarbonitrile	Styrene	γ-Butyrolactone	~0	0.93	
3-Chloro-1-bicyclo-butanecarbonitrile	Styrene	DMSO	0	≈1.9	Heterogeneous
3-Chloro-1-bicyclo-butanecarbonitrile	Styrene	γ-Butyrolactone	0.05	1.77	
Methyl-1-bicyclo-butanecarboxylate	Styrene	Methyl ethyl ketone	0.14	1.81	
1-Acetylbicyclo-butane	Styrene	DMSO	0.43	0.47	Heterogeneous
1-Acetylbicyclo-butane	Styrene	Methyl ethyl ketone	0.46	0.59	
1-Bicyclobutane-carbonitrile	Methyl methacrylate	γ-Butyrolactone	0.44	1.70	
1-Bicyclobutane-carbonitrile	Acrylonitrile	γ-Butyrolactone	0.50	1.10	
1-Bicyclobutane-carbonitrile	Ethyl vinyl ether	γ-Butyrolactone	2.30	0.03	



Reactivity Ratios. These were determined toward the polystyryl radical by conventional methods[4] and are presented in Table I. Representative Fineman–Ross plots are given in Figures 1 and 2.

The reactivity of various monomers toward polystyryl radical (Table II) was determined by taking the reciprocal of the reactivity ratio for styrene. Table III shows the reactivities toward polyacrylonitrile radical and Table IV toward poly-1-cyanocyclobutyl radical. The striking conclusion is that the bicyclobutanes are about as reactive in copolymerization as the corresponding vinyl monomers. This remarkable coincidence finds its basis in the high p character of the 1,3-single bond in these compounds.[5] Figure 3 shows an attempted linear free-energy diagram wherein the reactivity ratios of the bicyclobutane monomers (with

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(2) H. K. Hall, Jr., E. P. Blanchard, Jr., S. C. Cherkofsky, J. B. Sieja, and W. A. Sheppard, *J. Amer. Chem. Soc.*, **93**, 110 (1971) (accompanying article).

(3) H. K. Hall, Jr., C. D. Smith, E. P. Blanchard, Jr. S. C. Cherkofsky, and J. B. Sieja, *ibid.*, **93**, 121 (1971) (accompanying article).

(4) M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 269 (1950).

(5) (a) K. B. Wiberg, *Rec. Chem. Progr.*, **26**, 143 (1965); (b) M. Pomerantz and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **88**, 3970 (1966).

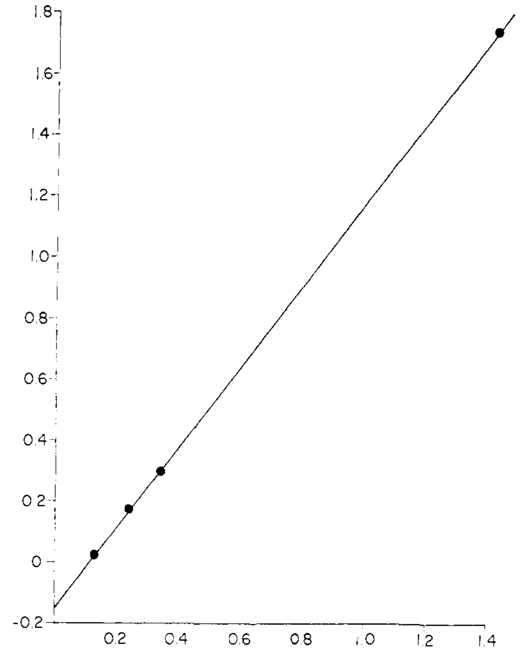

Figure 1. Reactivity ratio plot for copolymerization of 1-bicyclobutanecarbonitrile with styrene: abscissa, $(f_V/f_B)^2(F_B/F_V)$; ordinate, $(f_V/f_B)((F_V - F_B)/F_V)$.

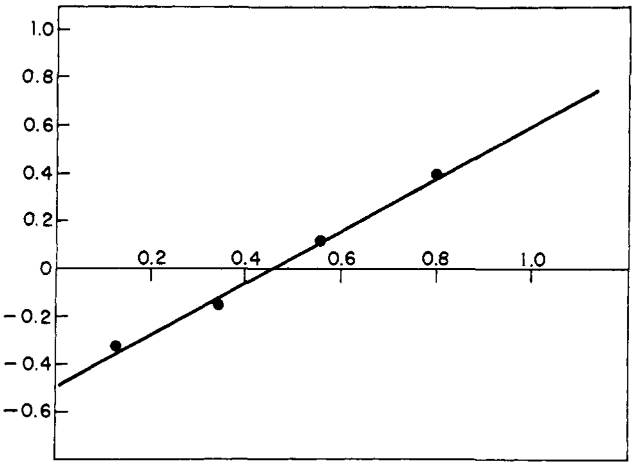

Figure 2. Reactivity ratio plot for copolymerization of 1-bicyclobutanecarbonitrile with acrylonitrile: abscissa, $(f_V/f_B)^2(F_B/F_V)$; ordinate, $(f_V/f_B)(F_V - F_B/F_V)$.

Table II. Reactivities of Monomers toward Polystyryl Radical

Monomer	Reactivity
Dimethyl fumarate	4.8
Fumaronitrile	4.4
Methyl vinyl ketone	3.4
Methacrylonitrile	3.3
Acrylonitrile	3.0
Methyl methacrylate	2.0
1-Acetylbicyclobutane	1.7
Methyl acrylate	1.3
1,3-Bicyclobutanedicarbonitrile	1.0
Styrene	1.0 (by definition)
1-Bicyclobutanecarbonitrile	0.71
Methyl-1-bicyclobutanecarboxylate	0.66
3-Chloro-1-bicyclobutanecarbonitrile	0.58
Dimethyl 1,3-bicyclobutanedicarboxylate	0.45

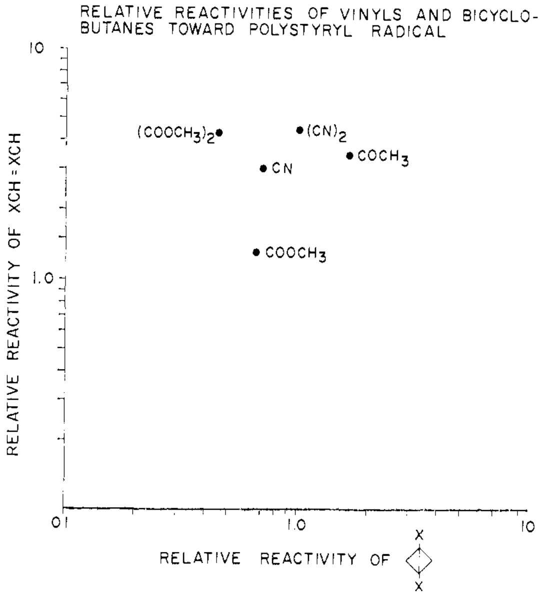

Figure 3. Attempted linear free-energy plot of reactivity ratios for bicyclobutane monomers (with styrene) *vs.* those of vinyl monomers: abscissa, k_{VV}/k_{VS}; ordinate, k_{BB}/k_{BS}.

Table III. Reactivities of Monomers toward Polyacrylonitrile Radical

Monomer	Reactivity
Styrene	14.2
Methyl methacrylate	10.0
Methacrylonitrile	2.32
1-Bicyclobutanecarbonitrile	2.0
Ethyl vinyl ether	1.42
Acrylonitrile	1.0

Table IV. Reactivities of Monomers toward Poly-1-cyanocyclobutyl Radical

Monomer	Reactivity
Styrene	8.3
Methyl methacrylate	2.3
1-Bicyclobutanecarbonitrile	1.00 (by definition)
Ethyl vinyl ether	0.34

styrene) are plotted against those of the corresponding vinyl monomers (trans where 1,2 disubstituted). The plot is not linear, but nevertheless reemphasizes the comparable reactivities of the two classes of monomer.

Chain Transfer. This phenomenon was demonstrated with isobutyraldehyde (Table V). This compound has a small chain-transfer constant[6] and can be used to control molecular weight in either solution or emulsion polymerization of 1-bicyclobutanecarbonitrile.

Molecular Weights and Distributions of Poly-1-bicyclobutanecarbonitrile. These are as high as those of ordinary vinyl polymers (Table VI). The range of molecular weight values recorded in Table VI is due to the discrepancy found for the light scattering (mol wt by blue light < mol wt by green light). We have related the molecular weights to the inherent viscosities by use of the Mark-Houwink-Sakurada

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[6] C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, pp 273-278.

Table V. Chain Transfer with Isobutyraldehyde in Polymerization of 1-Bicyclobutanecarbonitrile

Monomer	Wt % isobutyraldehyde[a]	η_{inh}[b] 0.1%, DMF	% yield
Solution Polymerizations in DMSO, 50°			
1-Bicyclobutanecarbonitrile		Gel	High
1-Bicyclobutanecarbonitrile	3.3	3.00	70
1-Bicyclobutanecarbonitrile	10.0	1.46	68
1-Bicyclobutanecarbonitrile	20.0	1.03	65
1-Bicyclobutanecarbonitrile		3.42	55
1-Bicyclobutanecarbonitrile	20	0.97	87
1-Bicyclobutanecarbonitrile	35	0.67	81
1-Bicyclobutanecarbonitrile	60	0.49	77
Emulsion Polymerizations, 50°			
Acrylonitrile–1-bicyclo-	0	3.06	93
butanecarbonitrile (50:50)	6	1.66	89
1-Bicyclobutanecarbonitrile	0	2.69	High
1-Bicyclobutanecarbonitrile	6	1.42	95

[a] Weight per cent isobutyraldehyde based on weight of monomer. [b] The slopes of intrinsic viscosity plots varied with molecular weight like those of conventional vinyl polymers.

Table VI. Molecular Weights of Poly-1-bicyclobutanecarbonitrile[a]

[η]	M_n osm mol wt[b]	M_w lt scatt mol wt[c] Blue light	Green light	Polydispersities (using blue light)
1.06	45,400	144,600	147,400	3.18
1.50	56,500	235,600	300,600	4.17
3.12	84,800	612,000	956,600	7.21

[a] Prepared by polymerization in tetramethylene sulfoxide solution. [b] 35°, N-methylpyrrolidone. [c] 28°, DMF.

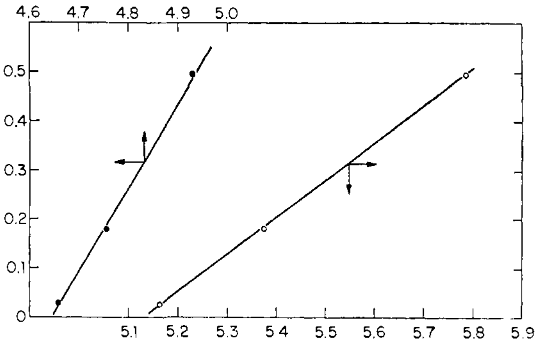

Figure 4. Staudinger plots for poly-1-bicyclobutanecarbonitrile: (top) abscissa (left line), log $\bar{M}_n$; (bottom) abscissa (right line), log $\bar{M}_w$; ordinate, log η_{int}.

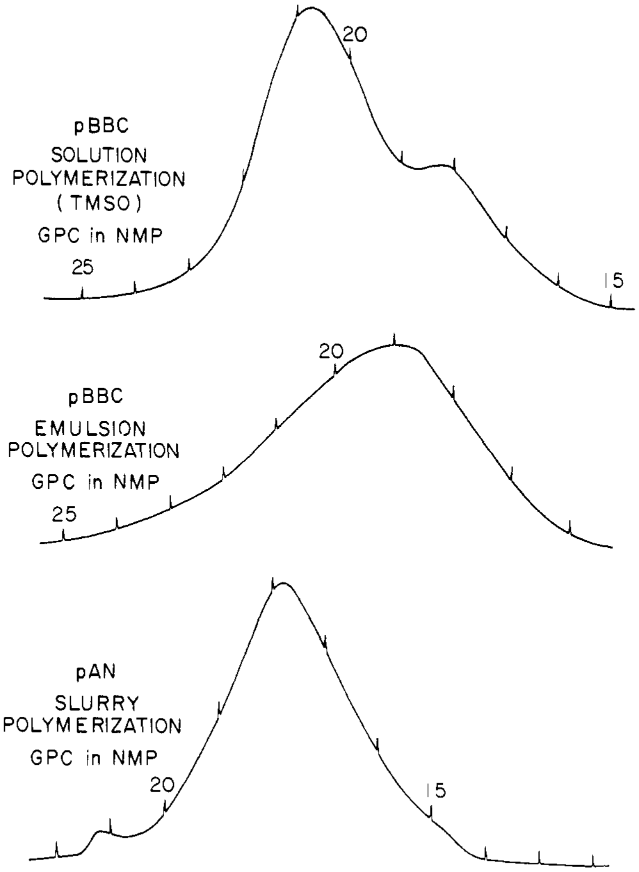

Figure 5. Gel permeation chromatograms for polybicyclobutanecarbonitrile and polyacrylonitrile: abscissa, elution volume; ordinate, differential refractive index; upper curve, made in tetramethylene sulfoxide solution; middle curve, made in emulsion; lower curve, made in slurry.

equation $[\eta] = KM_n^{\alpha}$ (Figure 4). The α value was close to the corresponding value for polyacrylonitrile[7,8]

	K	α
Acrylonitrile	4.43×10^{-4}	0.70
1-Bicyclobutanecarbonitrile	1.31×10^{-4}	0.76

The M_w/M_n values (polydispersities) were calculated from the molecular weight data in Table VI. Further information on molecular weight distribution was forthcoming through the use of gel permeation chromatography (gpc) on cross-linked polystyrene. Dilute solutions of the polymers in N-methylpyrrolidone were used to give the representative curves shown in Figure 5. Polymers prepared by emulsion and slurry had more symmetrical molecular weight distributions than those prepared in solution. As to the origin of the high molecular weight shoulders seen in the solution-polymerized samples, each polymer has a tertiary hydrogen in the polymer "backbone" subject to abstraction by growing polymer radicals or by initiators, *i.e.*, chain transfer to polymer which leads to branching. These branches, both short and long, contribute to greater than average molecular weights. When the medium viscosity is low and constant as in slurry and emulsion recipes, monomer can arrive at the growing end and chain transfer to polymer cannot compete well. However, in solution polymerization, because of high viscosities, the chain transfer to polymer problem does lead to the high molecular weight fractions. The inherent viscosities are also atypically higher for these cases. The ratio of propagation rate constant to transfer also plays an important role.[3]

Conclusions. The bicyclobutane monomers studied in this work behave in free-radical polymerizations astonishingly like vinyl monomers. The molecular weights of poly-1-bicyclobutanecarbonitrile are very high and can be controlled by chain transfer. Chain

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(7) C. H. Bamford and G. C. Eastmond in "Encyclopedia of Polymer Science and Technology," Vol. I, H. F. Mark, N. G. Gaylord, and N. M. Bikales, Ed., Interscience, New York, N. Y., 1964, pp 374–425.

(8) M. Kurata, M. Iwama, and K. Kamada, "Polymer Handbook," J. Brandrup, E. H. Immergut, and H. G. Elias, Ed., Interscience, New York, N. Y., 1967, p IV-23.

transfer to polymer occurs to a slight extent. Copolymerization parameters show that the bicyclobutanes are equally reactive to vinyl monomers in copolymerization, the reactivities all falling within a factor of 10 of each other and of the corresponding vinyl monomers. This demonstrates that these compounds constitute a new class of reactive monomer.

Experimental Section

Values for reactivity ratios in the literature vary from author to author, and corrections of analytical data are routinely made. Carbon, hydrogen, nitrogen, and oxygen percentages did not always add up to 100%. (Triplicate Dumas determinations required least sample and gave the most consistent results for N.) In such cases the per cent of each element found was then increased proportionately until the sum was 100%. As a check, styrene–acrylonitrile in DMSO gave results in good agreement with literature values:[9] $r_{\mathrm{styrene}} = 0.31$ (0.37) and $r_{\mathrm{AN}} = 0.13$ (0.07). Our reactivity ratios are of the same quality as those found in the literature.

The equation of Fineman and Ross[4] was used as

$$\left(\frac{f_V}{f_V}\right)\left(\frac{F_V - F_B}{F_V}\right) = \left(\frac{f_V}{f_B}\right)^2\left(\frac{F_B}{F_V}\right)(r_V - r_B)$$

where f_V = feed mole fraction of vinyl monomer and F_V = mole fraction of vinyl monomer in the resulting copolymer and correspondingly for the bicyclobutanes. Uncertainties in the intercept ($-r_B$) and the slope (r_V) should be about ±5%. Where comparison was made, homogeneous polymerizations gave the same reactivity ratios as polymerizations which became heterogeneous. In a typical run carrried to 1.5–3.6% conversion, AIBN, 0.0061 *M*, was the initiator in DMSO at 50° for 2 hr. These data are plotted in Figure 1. Similar data for the copolymerization of acrylonitrile with bicyclobutane-1-carbonitrile (1.5–2.5 hr; conversion 1.5–4.5%) are plotted in Figure 2.

Table VII

	In feed			In copolymer		
Sample	Mol of Sty	Mol of BBC	f_{Sty}	% N	Wt % Sty	F_{Sty}
A	0.01817	0.00771	0.702	2.88	83.74	0.796
B	0.01056	0.01403	0.429	5.57	68.55	0.623
C	0.01239	0.02111	0.370	6.21	64.94	0.586
D	0.00634	0.01707	0.271	7.44	57.99	0.512

The gel permeation chromatography experiments were done on 0.25% (w/v) solutions of the polymers in *N*-methylpyrrolidone on a series of 5 × 10⁶, 10⁵, and 10³ Å Styragel (cross-linked polystyrene) columns in a Waters Associates instrument at column temperatures of 90° and differential refractometer detector temperature at 75°.

(9) H. Mark, B. Immergut, E. H. Immergut, L. J. Young, and K. I. Benynon, "Polymer Handbook," ref 7, pp II-144–II-155.

Thermochemistry of Strained-Ring Bridgehead Nitriles and Esters

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Abstract: Enthalpies of formation of a variety of potentially polymerizable bicyclic bridgehead nitriles and esters were determined. Because plots of these enthalpies of formation against those for the corresponding hydrocarbon were linear with unit slope, specific stabilizations or destabilizations were minor. Replacement of H by CN in an organic molecule made $\Delta H_{f,g}{}^{\circ}{}_{298}$ more positive by 24 kcal mol^{-1}; by $COOCH_3$, more negative by 89 kcal mol^{-1}. An alternative derivation of the Flory equation, which relates enthalpies of hydrogenation to those of polymerization, is given. Using this alternative approach, enthalpies of polymerization were calculated for various strained ring systems. These agreed well with the calculated release of strain energy and lay in the order: bicyclo[2.2.0]pentanes > bicyclobutanes > bicyclo[3.1.0]hexanes > ethylenes.

Studies of the polymerization of substituted small strained carbocyclic rings showed that monomers containing bridgehead cyano and ester substituents polymerized most satisfactorily.[2,3] We have determined $\Delta H_{f,g}{}^{\circ}{}_{298^{\circ}}$, the standard enthalpies of formation, for various small-ring nitriles and esters to calculate the thermodynamics of their polymerization and place ring-opening polymerization of a strained C—C single bond on a quantitative basis.

Results

Enthalpies of combustion were determined with a precision Bureau of Mines type rotating bomb calorimeter. From them and the corresponding enthalpies of vaporization, enthalpies of formation in the gas phase at 298°K have been calculated. The results are given in Table I. We redetermined the enthalpies of formation of a few compounds for which data were already in the literature to check our technique; agreement was generally good. Precision was usually ±0.04%.

Correlation with Data for Corresponding Hydrocarbons. Table II summarizes the enthalpies of formation of the nitriles and the corresponding hydrocarbons, and Figure 1 plots these quantities against each other. The plot is linear, with the expected unit slope, and shows that replacement of H by CN in a simple organic molecule raises $\Delta H_{f,g}{}^{\circ}{}_{298}$ by +24 kcal mol^{-1}. This is consistent with the value of +27.5 kcal mol^{-1} recently found by Koniek, Prochazka,

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(2) H. K. Hall, Jr., E. P. Blanchard, Jr., S. C. Cherkofsky, J. B. Sieja, and W. A. Sheppard, *J. Amer. Chem. Soc.*, **93**, 0000 (1971).

(3) H. K. Hall, Jr., C. D. Smith, E. P. Blanchard, Jr., S. C. Cherkofsky, and J. B. Sieja, *ibid.*, **93**, 121 (1971).