Copolymerization of 4-Cyclopentene-1,3-dione with Styrene*

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Synopsis

The copolymerization of 4-cyclopentene-1,3-dione (D) with styrene (S) is reported. The copolymers were prepared by heating sealed tubes containing the monomer feeds and azobisisobutyronitrile. The copolymers exhibited infrared bands for the phenyl and β-diketone groups, indicating that copolymerization had occurred. The copolymers were completely insoluble in all solvents. Some swelling was observed in tetrahydrofuran, nitrobenzene, and aqueous sodium hydroxide. From the compositions of the copolymers, as determined from the carbon and hydrogen analyses, it was found that the copolymers were about 40 mole-% styrene over an appreciable range of feed compositions (0.1–0.6 mole fraction styrene). The results at styrene feeds <0.5 were in general agreement with the equation: $d[\mathrm{D}]/d[\mathrm{S}] = 1^{1}/_{2} + (k_{DD}/2k_{DC}K[\mathrm{S}])$. This equation was derived on the basis of monomer complex (C) participating in the propagation and a penultimate effect preventing the occurrence of a sequence of three dione units.

INTRODUCTION

The copolymerization of 4-cyclopentene-1,3-dione with acrylonitrile and methyl methacrylate was reported in a previous paper of this series.[1] These copolymerizations proceeded normally, allowing the determination of reactivity ratios for each system and the assignment of Q and e values to 4-cyclopentene-1,3-dione. In this paper the copolymerization of 4-cyclopentene-1,3-dione with styrene is reported, and a possible correlation of the results with the copolymerization equation, through considerations of complex formation and penultimate unit effects, is suggested.

EXPERIMENTAL

Materials

The preparation and purification of 4-cyclopentene-1,3-dione was described in the previous communication.[1]

Styrene (The Bordon Chemical Company) was distilled under nitrogen at 72°C./65 mm. after the addition of a trace of sulfur. A middle fraction was collected and used immediately.

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* Taken from the Ph.D. Dissertation of F. Lynn Hamb (1963).
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Polymerization Procedure

The desired ratio of styrene and 4-cyclopentene-1,3-dione was dissolved in the minimum amount of pure dry benzene. The solution was placed in a thick-walled tube and 0.05 mole-% of the charge of azobisisobutyronitrile was added. After degassing by alternate cooling and warming under a low pressure of nitrogen, the tube was sealed at 0.1–0.2 mm. and placed in a constant temperature bath at $50 \pm 0.1°C$. The contents were stirred with a small bar magnet until the reaction had proceeded to an extent of 2 or 3%, as estimated by the precipitation of the insoluble copolymer. The tube was cooled to room temperature and opened. The mixture was poured into a nonsolvent consisting of methanol for high styrene content, ethyl ether for low styrene content, or a mixture of methanol and ethyl ether for intermediate styrene content, and the flocculent tan copolymer was allowed to settle. The polymer was collected by filtration, washed with ethyl ether, dried in air at room temperature, and weighed to determine the per cent conversion.

Characterization of the Copolymers

The characteristic infrared absorptions of the phenyl group at 1650 cm.$^{-1}$ and of the β-diketone group at 1580 cm.$^{-1}$ indicates that both styrene and 4-cyclopentene-1,3-dione have entered the copolymer.

The solubility properties of all copolymers, regardless of the feed compositions, are nearly identical. Common solvents such as benzene, toluene, acetone, methyl ethyl ketone, diethyl carbonate, dimethylformamide, dimethyl sulfoxide, and chloroform have no noticeable effect on the copolymers. They are swollen slightly by the action of tetrahydrofuran, nitrobenzene, and aqueous sodium hydroxide. Molecular weight studies were not feasible because of the extreme insolubility of the copolymers. The

TABLE I
Reactivity Ratio Data for the Copolymerization of Styrene(S) and
4-Cyclopentene-1,3-dione(D)

f_1 Mole fraction S in feed	Time, min.	Conversion, %	Analysis		F_1 Mole fraction S in copolymer
			C, %	H, %	
0.96[a]	150	1.54	83.09	7.82	0.61
0.90[a]	50	0.87	78.51	6.44	0.52
0.80[a]	130	2.50	77.34	7.11	0.48
0.65[b]	100	1.39	75.87	6.40	0.43
0.35[b]	15	1.46	74.81	7.62	0.40
0.25[b]	60	2.35	74.94	6.35	0.40
0.15[b]	150	2.24	73.16	6.17	0.34
0.08[b]	220	2.06	74.21	6.31	0.37
0.04[b]	45	2.15	73.33	6.24	0.35

[a] No solvent.
[b] Benzene solvent.

swelling action of sodium hydroxide solution indicates the presence of weakly acidic structures characteristic of enolic β-diketones. The swelling effect of tetrahydrofuran and nitrobenzene suggests that there may be cross-linking between polymer chains, perhaps through chain transfer reactions with the active hydrogens of the β-diketone structure. The amorphous, hard polymers are not fusible when heated in a Bunsen flame, but form a brown granular material.

Analysis of the Copolymers

The copolymers were crushed to a fine powder, extracted with refluxing benzene in a Soxhlet apparatus for 8 hr., and dried in air under reduced pressure for 6 hr. The composition of each sample was calculated from the elemental analysis for carbon and hydrogen as determined by Galbraith Laboratories, Inc., Knoxville, Tennessee. The results are reported in Table I.

RESULTS

The mole fraction of styrene in the copolymer (F_1) is plotted in Figure 1 as a function of the mole fraction of styrene in the feed (f_1). Treatment of the copolymer equation by the method of Mayo and Lewis[2] (Fig. 2) and by the method of Fineman and Ross[3] (Fig. 3) afforded values of r_1 and r_2 (Table II).
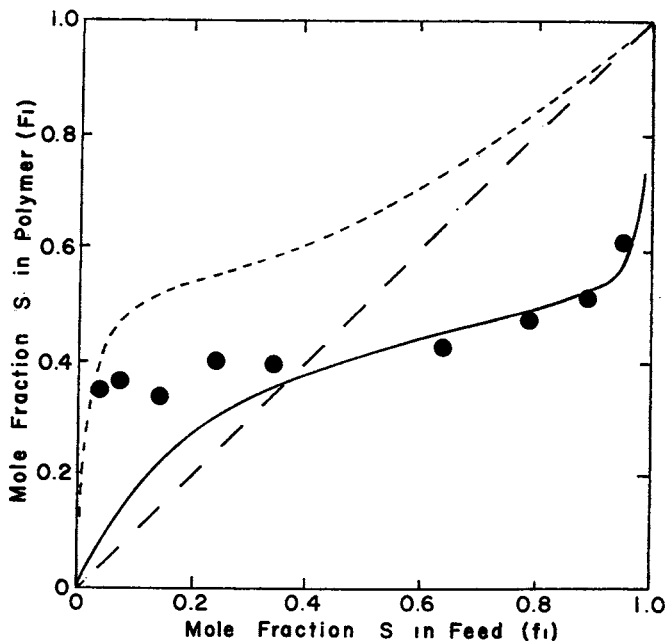

Fig. 1. Copolymerization of styrene (S) with 4-cyclopentene-1,3-dione (D): (——) calculated for $r_1 = 0.02$, $r_2 = 0.4$; (- -) calculated for $r_1 = 1.5$, $r_2 = 0.033$ as determined from the Q and e values of the monomers.
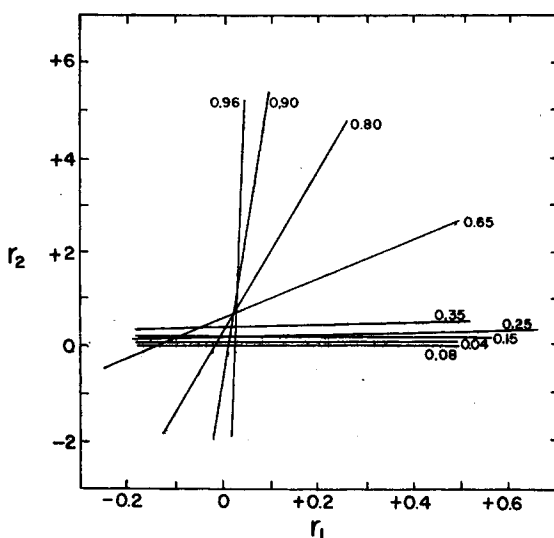
Fig. 2. Mayo-Lewis plot for determining reactivity ratios. The number at each line is the feed composition in mole fraction of styrene. $r_1 = 0.015 \pm 0.015$; $r_2 = 0.4 \pm 0.35$.
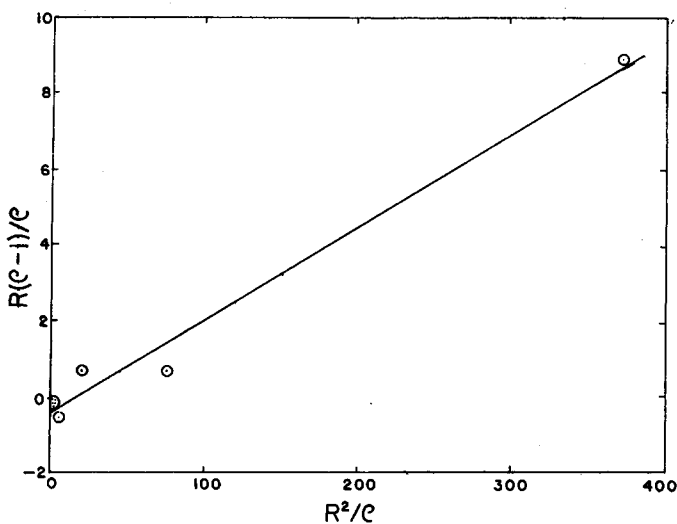

Fig. 3. Fineman-Ross plot for determining reactivity ratios. $r_1 = 0.024$; $r_2 = 0.415$.

By using the IBM 1620 digital computer, numerous combinations of reactivity ratios from $r_1 = 0$–0.15 and $r_2 = 0.01$–0.7 were tested in the copolymer equation, but no combination was found which produced a curve fitting the data over the entire composition range. The unbroken curve of Figure 1, obtained from the reactivity ratios listed in Table II, seemed to be about the best overall fit. Agreement is good in the region above 0.5

TABLE II
Reactivity Ratios for the Copolymerization of
Styrene(M_1)–4-Cyclopentene-1,3-dione(M_2)

| Method	r_1	r_2
Mayo-Lewis	0.015 ± 0.015	0.4 ± 0.35
Fineman-Ross	0.024	0.415
Curve fitting	0.02	0.4
Alfrey-Price	1.5	0.033

mole fraction of styrene in the feed, but considerable departure from the curve is observed at concentrations below this value.

From the Q and e values of 4-cyclopentene-1,3-dione ($Q = 0.20$, $e = +1.42$)[1] and styrene ($Q = 1.0$, $e = -0.8$),[4] reactivity ratios were calculated according to the method of Alfrey and Price.[5] These values of r_1 and r_2 (Table II) and the resulting copolymer composition curve (broken curve in Fig. 1) are not consistent with the observed results.

DISCUSSION

The failure to reproduce the experimental curve by the curve-fitting method and the considerable divergence between the experimental curve and the curve predicted by the Q and e values indicate that the copolymer composition equation does not apply in a simple way to the styrene(S)–4-cyclopentene-1,3-dione(D) system. This is further indicated by the ability to fit a curve to the experimental data at high styrene, but not at low styrene feeds. Also, in Figure 2, the r_2 versus r_1 lines seem to fall into two groups: high styrene feeds (0.96, 0.90, 0.80, and 0.65) and low styrene feeds (0.35, 0.25, 0.15, 0.08, and 0.04).

If the structure of the copolymers approached perfect alternation of the monomer units (structure I), F_1 would be 0.5. If II or III represented the structure, F_1 would be 0.33 or 0.40, respectively.

$$+S-D+_n \qquad +D-S-D-)_n \qquad +D-S-D-S-D+_n$$
$$I \qquad\qquad II \qquad\qquad III$$
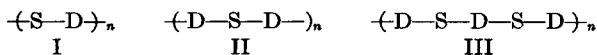
The occurrence of F_1 values between 0.3 and 0.4 in the region of low to medium values of f_1 (Fig. 1) indicates that the copolymers are partially alternating, and that the average structure is best represented by II or III. The results may be compared with those of Fordyce and Ham,[6] who found that in the copolymerization of the styrene–fumaronitrile system the fumaronitrile content of the copolymers approached 40 mole-% with increasing concentration in the feed.[7] The dione case is different in that it is the styrene concentration that approaches 40 mole-%.

The copolymerization of styrene with sulfur dioxide and of ethylene with carbon monoxide, both of which provide highly alternating copolymers have been interpreted by Barb[8,9] on the basis of a copolymerization between a 1:1 complex and the monomer present in the greater amount. In the case of the styrene(S)–sulfur dioxide (SO_2) system, a 1:1 complex of

TABLE III
Feed and Copolymer Composition Data for the System
Styrene(S)–4-Cyclopentene-1,3-dione(D)

	Monomer feed			Copolymer	
f_1	[S], mole/l.	[D], mole/l.	1/[S]	F_1	n
0.35	2.08	3.87	0.418	0.40	1.53
0.25	0.97	2.89	1.03	0.40	1.51
0.15	0.64	3.62	1.56	0.34	1.94
0.08	0.35	3.99	2.86	0.37	1.68
0.04	0.17	4.18	5.88	0.35	1.90

the two monomers copolymerized with styrene in a perfectly alternating fashion to form a copolymer having an average structure:

$$-[S-SO_2]---S-_n$$
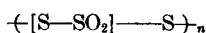
where the brackets enclose the complex residue. By writing the individual rate equations in terms of a 1:1 styrene–sulfur dioxide complex (C) and through an assumption that the reaction of complex radical with complex was negligible, Barb derived the expression

$$n = d[S]/d[SO_2] = 2 + (k_{SS}/k_{SC}K[SO_2]) \tag{1}$$

where K is the equilibrium constant for formation of the complex:

$$[C] = K[S][SO_2] \tag{2}$$

The plot of n versus $1/[SO_2]$ was found to be linear with an intercept of 2.

Walling[10] has shown that an equation of the same kinetic form as that of Barb can be derived through a sequence which includes two reversible steps and a penultimate unit effect. The fit of the data to both of these equivalent kinetic schemes makes difficult a choice between the two proposals.

If the styrene(S)–4-cyclopentene-1,3-dione(D) system in the region of low styrene concentration is analogous to styrene–sulfur dioxide, a plot of
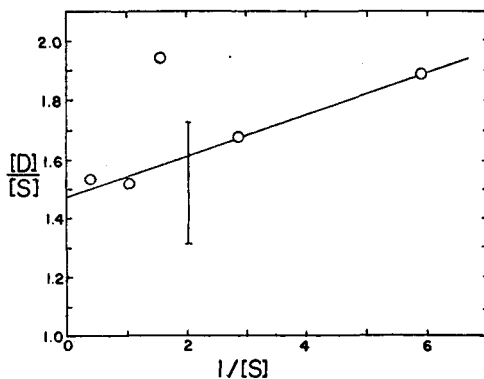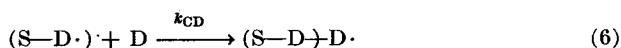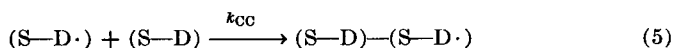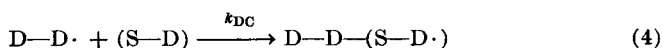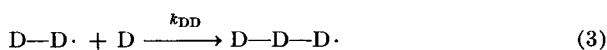

Fig. 4. Plot of [D]/[S] in the polymer as a function of 1/[S] in the feed according to eq. (9). The bracket spans a range equivalent to ±1% error in the carbon analysis.

n, the ratio of the dione to styrene in the copolymer, as a function of $1/[S]$ at constant dione concentration should be linear with an intercept of 2. The information required for this plot is given in Table III.

Although the dione concentrations are not constant, they are close enough to test this proposal. The plot of n versus $1/[S]$ (Fig. 4) is linear within reasonable experimental error. However, since the n intercept is not 2, but 1.48, the treatment of Barb[8] or Walling[10] does not apply to this system.

Retaining the idea of the complex and writing the kinetic equation for the copolymerization in terms of the individual structural units, where the complex or complex residue in the polymer is enclosed in parentheses, eqs. (3)–(6) are obtained for the region of low styrene concentration ($f_1 < 0.5$).

$$D\text{—}D\cdot\ +\ D\ \xrightarrow{\ k_{DD}\ }\ D\text{—}D\text{—}D\cdot \tag{3}$$

$$D\text{—}D\cdot\ +\ (S\text{—}D)\ \xrightarrow{\ k_{DC}\ }\ D\text{—}D\text{—}(S\text{—}D\cdot) \tag{4}$$

$$(S\text{—}D\cdot)\ +\ (S\text{—}D)\ \xrightarrow{\ k_{CC}\ }\ (S\text{—}D)\text{—}(S\text{—}D\cdot) \tag{5}$$

$$(S\text{—}D\cdot)\ +\ D\ \xrightarrow{\ k_{CD}\ }\ (S\text{—}D)\text{—}D\cdot \tag{6}$$

This scheme includes the assumption that styrene enters the copolymer only through complex and that the complex units add to the growing chain through the styrene end of the complex, as would be predicted on the basis of steric effects.

Assuming for the moment that penultimate group effects are negligible, then the rates of eqs. (4) and (5) would be equal, since both involve the addition of the complex to the same chain radical. Thus:

$$k_{DC}[D\cdot][C]\ =\ k_{CC}[C\cdot][C] \tag{7}$$

The copolymer equation can now be written as:

$$d[D]/d[C]\ =\ (k_{DD}[D\cdot][D]\ +\ k_{CD}[C\cdot][D])/2k_{DC}[D\cdot][C] \tag{8}$$

Elimination of radical concentration with the steady-state expression, conversion of the left-hand side to a ratio of the structural units, and replacement of [C] on the right-hand side with the equilibrium expression for the formation of the complex leads to eq. (9).

$$n\ =\ d[D]/d[S]\ =\ 1\ +\ (d[D]/d[C])\ =\ 1\tfrac{1}{2}\ +\ (k_{DD}/2k_{DC}\ K\ [S]) \tag{9}$$

With the exception of one point, the results plotted in Figure 4 are in general agreement with the requirements of eq. (9).

On this same basis, eqs. (3) and (6) might also be expected to be equal, since both equations represent the addition of the dione monomer to dione chain radicals. The result would be, however, that the rates of all four of the competing reactions, eqs. (3)–(6), would be equal, and eq. (8) would reduce to $n = 2$, which is inconsistent with the observed results.

If the previous reasoning concerning the mode of addition of this complex is correct, the inequality of eqs. (3) and (6) can be interpreted on the

basis of a penultimate unit effect of considerably greater significance than that expected in the case of eqs. (4) and (5). This effect can be attributed to steric factors which suppress the addition of a dione unit to a chain radical already ending in two dione units, eq. (3). A strong steric effect operating in eqs. (4) and (5), the addition of a relatively nonbulky styrene end of the complex to the chain, would not be as important. A detectable penultimate effect in this copolymerization is not unreasonable in view of the results of Barb[11] and Ham.[7,12,13]

The data as plotted in Figures 1 and 4 are consistent with the average structure III for the copolymer in the region of $0.5f_1$ with a trend directed toward structure II with decreasing styrene in the feed.

Correlation of the data for high styrene feeds with the proposed 1:1 complex is not as successful as for low styrene feeds. The Mayo-Lewis plot (Fig. 2) in which the reactions were assumed to involve styrene and 4-cyclopentene-1,3-dione monomers shows a well-defined intersection for the high styrene feeds (0.96, 0.90, 0.80, 0.65) corresponding to $r_1 = 0.03$ and $r_2 = 0.8$. The high value of the apparent reactivity ratio, r_2, is difficult to explain in view of the recognized low reactivity of the dione.[1]

With more data in the high styrene region, correlation with the sequence distribution treatment as proposed by Berger and Kuntz[14] and supported by Ang and Harwood[15] to distinguish between the terminal model and the penultimate model for copolymerization might be feasible. If the dione system is at all similar to the case of maleic anhydride, then such an analysis might easily indicate the simple terminal model of copolymerization. However, the proposal of a penultimate effect at low styrene feeds would not be jeopardized, since the penultimate effect as proposed here operates only to prevent a sequence of three dione units from occurring, an unlikely event in any case at high styrene feeds. A knowledge of the number of dione units in sequences for copolymers prepared at various feed ratios would be most valuable in attempting to support the penultimate group effect.

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Résumé

On décrit la copolymérisation du 4-cyclopentène-1,3-dione (D) avec le styrène (S). Les copolymères sont préparés en chauffant des tubes scellés contenant les mélanges des monomères et de l'azobisisobutyronitrile. Les copolymères montrent dans l'infrarouge des bandes caractéristiques du groupe phényle et du groupe β-dicétone, ce qui indique que la copolymérisation a eu lieu. Les copolymères sont tout-à-fait insolubles dans tous les solvants. On a observé un léger gonflement dans le tétrahydrofurane, le nitrobenzène, et l'hydroxyde de sodium en solution aqueuse. A partir de la composition des copolymères, déterminée par des analyses de carbone et d'hydrogène, on montre que les copolymères contiennent à peu près 40 mole-% de styrène dans un domaine assez étendu de compositions du mélange de départ (fraction molaire de styrène 0.1 à 0.6) Les résultats pour des compositions en styrène <0.5 sont en bon accord avec l'équation: $d[D]/d[S] = 1\frac{1}{2} + k_{DD}/2\,k_{DC}K[S]$ Cette équation est obtenue sur la base de l'existence d'un complexe monomérique (C) participant à la propagation et d'un effet de l'unité pénultième qui empêcherait la formation d'une séquence composé de trois unités dione.

Zusammenfassung

Es wird über die Copolymerisation von 4-Cyclopenten-1,3-dion (D) mit Styrol (S) berichtet. Die Copolymeren wurden durch Erhitzung des Monomeransatzes mit Azobisisobutyronitril in zugeschmolzenen Röhren dargestellt. Die Copolymeren weisen für Phenyl- und β-Diketongruppen charakteristische Infrarotbanden auf, was für den Eintritt einer copolymerisation spricht. Die Copolymeren waren in allen Lösungsmitteln völlig unlöslich, eine gewisse Quellung wurde in Tetrahydrofuran, Nitrobenzol und wässrigem Natiumhydroxyd beobachtet. Die Zusammensetzung der Copolymeren wurde durch Kohlenstoff- und Wasserstoffanalysen bestimmt und zeigte, dass die Copolymeren über einen betrachtlichen Zusammensetzungsbereich des Monomeransatzes (0,1−0,6 Molenbruch Styrol) einen Gehalt von etwa 40 Mol-% Styrol besassen. Die Ergebnisse bei einem Styrolgehalt des Ansatzes < 0,5 waren im allgemeinen mit der Gleichung $d[D]/d[S] = 1\frac{1}{2} + k_{DD}/2k_{DC}K[S]$ in Übereinstimmung. Diese Gleichung wurde unter der Annahme abeleitet, dass ein Monomerkomplex (C) am Wachstum teilnimmt und ein Einfluss des vorletzten Gliedes das Auftreten einer Sequenz von drei Dioneinheiten verhindert.