Copolymerization of 4-Cyclopentene-1,3-dione with p-Chlorostyrene and Vinylidene Chloride

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Synopsis

The copolymerization of 4-cyclopentene-1,3-dione (M_2) with p-chlorostyrene and vinylidene chloride is reported. The copolymers were prepared in sealed tubes under nitrogen with azobisisobutyronitrile initiator. Infrared absorption bands at 1580 cm.$^{-1}$ revealed the presence of a highly enolic β-diketone and indicated that copolymerization had occurred. The copolymer compositions were determined from the chlorine analyses and the reactivity ratios were evaluated. The copolymerization with p-chlorostyrene (M_1) was highly alternating and provided the reactivity ratios $r_1 = 0.32 \pm 0.06$, $r_2 = 0.02 \pm 0.01$. Copolymerization with vinylidene chloride (M_1) afforded the reactivity ratios $r_1 = 2.4 \pm 0.6$, $r_2 = 0.15 \pm 0.05$. The Q and e values for the dione ($Q = 0.13$, $e = 1.37$), as evaluated from the results of the vinylidene chloride case, agree closely with the previously reported results of copolymerization with methyl methacrylate and acrylonitrile and confirm the general low reactivity of 4-cyclopentene-1,3-dione in nonalternating systems.

INTRODUCTION

In previous papers of this series,[1,2] 4-cyclopentene-1,3-dione was shown to copolymerize readily with several common monomers. With methyl methacrylate and acrylonitrile the copolymers were always richer in co-monomer than the feed over the entire feed composition range.[1] With styrene highly alternating copolymers were obtained.[2] This behavior of the dione is generally consistent with that of other cyclic monomers of similar structure.

An unusual feature of the copolymerization with styrene was that the copolymer composition curve approached 0.4 mole fraction styrene, rather than the simple alternation value of 0.5. Copolymerization involving a complex between styrene and the dione was suggested as a possible explanation for this behavior. To test the possibility that this effect was due merely to a distortion of the analytical data by the presence of fragments of the initiator (azobisisobutyronitrile), a distinct possibility since the molecular weight appeared to be low, the work was repeated and the data corrected for initiator from the nitrogen content. Although the corrections tended to raise the curve somewhat toward 0.5 mole fraction, the change was slight, and essentially the same copolymer composition curve was obtained as before.

To find out if this effect would be carried over to other cases of high alternation, the copolymerization of the dione with p-chlorostyrene was studied. A particular advantage of this system is that the copolymer compositions, as determined from the chlorine analyses, would be less affected by initiator fragments, trapped solvent, etc., than the styrene system, which involved carbon analyses.

Copolymerization studies of the dione with vinylidene chloride were also carried out to learn more of the general reactivity of the dione monomer itself, and to provide further information concerning the steric and electronic forces controlling the polymerization of cyclic monomers.

EXPERIMENTAL

Materials

The monomer, 4-cyclopentene-1,3-dione, was prepared from cyclopentenediol[3] and recrystallized three times from ether to give yellow crystals, m.p. 34°C. Vinylidene chloride and benzene were distilled under nitrogen and middle fractions were collected for use. The p-chlorostyrene was distilled under reduced pressure.

Polymerization Procedure

The desired molar ratios of 4-cyclopentene-1,3-dione and the comonomer were prepared and placed in thick-walled tubes along with about 10 ml. of benzene and 1 mole-% of azobisisobutyronitrile. The oxygen was removed by the usual degassing technique with a nitrogen flush, and the tubes were then sealed under about 1 mm. pressure of nitrogen. The polymerizations were carried out in a constant temperature bath with agitation.

The copolymers of p-chlorostyrene were prepared at 50°C. Precipitation of the copolymers occurred during the polymerization. After the polymerizations had proceeded to about 5–15% conversion, the tubes were opened and the contents were diluted with methanol (low dione feeds) or diethyl ether (high dione feeds). The solid granular polymers were collected, washed with benzene and ether, and dried under reduced pressure for several days.

The copolymers of vinylidene chloride were prepared at 65°C. The copolymers from the low dione feeds were soluble, and the solutions became viscous during the polymerizations. At high dione feeds the copolymers partially precipitated. After appropriate times the polymerizations were terminated, and the copolymers were caused to precipitate by the addition of methanol (low dione feeds) or diethyl ether (high and intermediate dione feeds). The polymers were collected, washed either with methanol or ether, and dried for several days under reduced pressure. Since the solubility characteristics of the copolymers vary considerably with the composition, further purification by reprecipitation was not performed in order to avoid possible separation and loss of some copolymer fractions.

Characterization and Analysis

All of the copolymers possessed strong infrared absorption at 1580 cm.$^{-1}$, characteristic of the highly enolic form of the β-diketone group.

The copolymers of p-chlorostyrene were insoluble or only very slightly soluble in the common solvents. The solubility of the vinylidene chloride copolymers was a function of the composition. At high dione content, the copolymers were insoluble in acetone and dioxane but were soluble in DMSO and DMF. At intermediate dione content, the copolymers were soluble in all four of these solvents. At low dione content the copolymers were insoluble but exhibited some swelling. All copolymers showed low solubility in methanol, carbon tetrachloride and chloroform.

The copolymers were analyzed for chlorine and the copolymer compositions were determined. The feed–copolymer composition data are re-

TABLE I
Data for Copolymerization
of p-Chlorostyrene (M_1) with 4-Cyclopentene-1,3-dione (M_2)

Mole fraction M_1 in feed f_1	Time, min.	Conversion, %	Analysis for Cl, %[a]	Mole fraction M_1 in polymer F_1
0.05	120	9.50	12.48	0.40
0.10	120	16.28	14.23	0.46
0.20	120	14.68	16.34	0.55
0.30	120	11.35	15.72	0.53
0.40	120	17.68	15.72	0.53
0.50	90	14.40	16.12	0.54
0.70	90	11.20	18.36	0.64
0.80	90	5.05	19.72	0.70

[a] Crobaugh Laboratories, Inc., Charleston, West Virginia.

TABLE II
Data for Copolymerization
of Vinylidene Chloride (M_1) with 4-Cyclopentene-1,3-dione (M_2)

Mole fraction M_1 in feed f_1	Time, min.	Conversion, %	Analysis for Cl, %[a]	Mole fraction M_1 in polymer F_1
0.05	90	3.91	16.65	0.23
0.10	90	4.20	24.93	0.34
0.20	150	12.83	37.12	0.50
0.30	150	15.54	42.87	0.58
0.40	150	7.05	59.34	0.80
0.50	150	6.44	62.97	0.86
0.60	150	17.42	61.70	0.84
0.70	150	13.15	68.27	0.93
0.80	15	1.86	66.21	0.90
0.90	15	2.42	68.90	0.94

[a] Galbraith Laboratories, Inc., Knoxville, Tennessee.

ported in Table I for copolymerization with p-chlorostyrene and in Table II for copolymerization with vinylidene chloride.

RESULTS

Copolymerization with p-Chlorostyrene

In Figure 1 the mole fraction p-chlorostyrene (M_1) in the copolymer F_1 is plotted against the mole fraction in the feed f_1. Solution of the copolymer equation by the Fineman-Ross[4] and Mayo-Lewis[5] methods are shown in Figures 2 and 3, respectively. From various r_1, r_2 combinations taken from
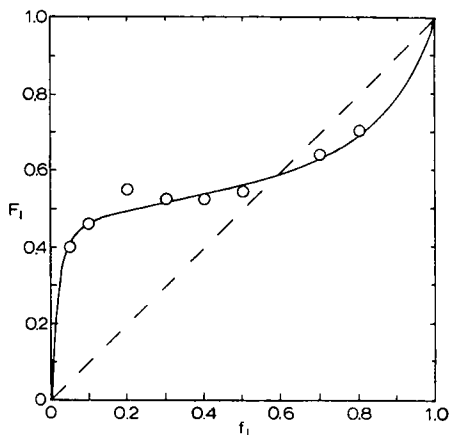

Fig. 1. Feed–copolymer composition plot for p-chlorostyrene (M_1), 4-cyclopentene-1,3-dione (M_2). The curve is for $r_1 = 0.32$, $r_2 = 0.02$.
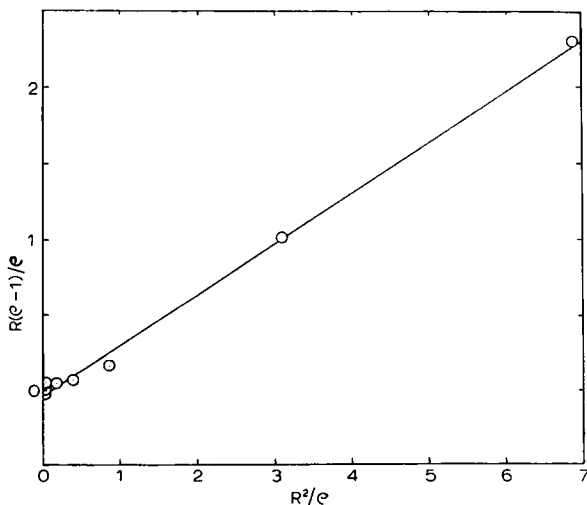

Fig. 2. Fineman-Ross plot for the copolymerization of p-chlorostyrene (M_1) with 4-cyclopentene-1,3-dione (M_2).
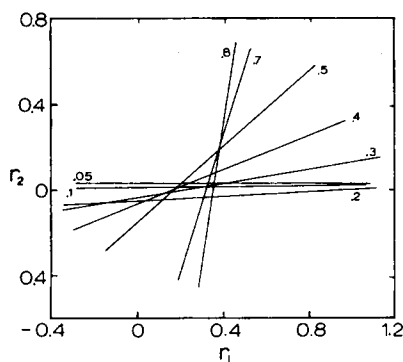
Fig. 3. Mayo-Lewis plot for the copolymerization of p-chlorostyrene (M_1) with 4-cyclopentene-1,3-dione (M_2).

within the area of intersection of Figure 3, copolymer composition curves were prepared with the aid of an IBM 7040 computer. The one which appeared to be the most accurate representation of the experimental data is shown in Figure 1. The reactivity ratios as determined by the three methods are tabulated in Table III.

TABLE III
Reactivity Ratios for the Copolymerization of
p-Chlorostyrene (M_1) with 4-Cyclopentene-1,3-dione (M_2)

Method	r_1	r_2
Fineman-Ross	0.34	0.03
Mayo-Lewis	0.30 ± 0.06	0.02 ± 0 01
Curve fitting	0.32	0.02 ± 0.01
Average	0.32 ± 0.06	0.02 ± 0.01

Copolymerization with Vinylidene Chloride

The feed–copolymer composition curve for the vinylidene chloride (M_1)–dione (M_2) system is shown in Figure 4. The data, plotted according to the Fineman-Ross method, were somewhat too scattered to provide reliable values for the reactivity ratios from a least-squares treatment over the entire range. However, a plot of the first four points ($f_1 = 0.05$–0.3), Figure 5, was reasonably linear, and values for the reactivity ratios were obtained (Table IV). Since the form of this portion of the copolymer curve

TABLE IV
Reactivity Ratios for the Copolymerization of
Vinylidene Chloride (M_1) and 4-Cyclopentene-1,3-dione (M_2)

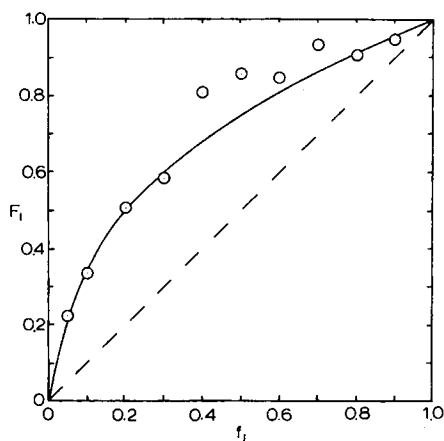| Method	r_1	r_2
Fineman-Ross[a]	2.1	0.15
Mayo-Lewis	2.4 ± 0.6	0.15 ± 0.05

[a] Based upon data for $f_1 = 0.05$–0.3.

Fig. 4. Feed–copolymer composition plot for vinylidene chloride (M_1), 4-cyclopentene-1,3-dione (M_2). The curve is for $r_1 = 2.4$, $r_2 = 0.15$.
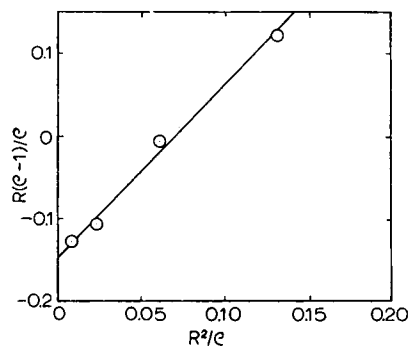

Fig. 5. Fineman-Ross plot for the copolymerization of vinylidene chloride (M_1) with 4-cyclopentene-1,3-dione (M_2).
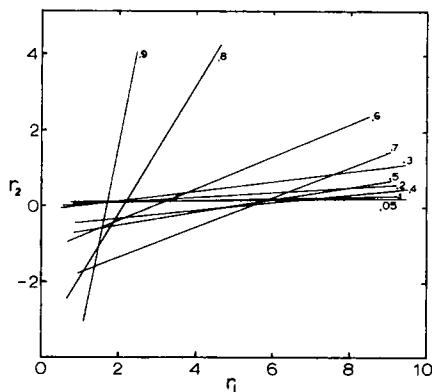

Fig. 6. Mayo-Lewis plot for the copolymerization of vinylidene chloride (M_1) with 4-cyclopentene-1,3-dione (M_2).

(Fig. 4) is determined largely by r_2 and affected little by small changes in r_1, a fairly accurate r_2 value may be obtained by this means. On the other hand, the r_1 value from the Fineman-Ross plot is not very accurate and is useful only as an estimate of the approximate magnitude.

Solution of the copolymer equation by the Mayo-Lewis method is shown in Figure 6. Here again a unique soution is difficult, since there appears to be two areas of maximum intersections, one for $r_1 = 2$ and another for $r_1 = 6$. In view of the approximate value for r_1, obtained from the Fineman-Ross treatment, the intersection at $r_1 = 2$ is the more reasonable value. From this area of intersection the r_1, r_2 values were evaluated (Table IV). Since the Mayo-Lewis values also seemed to provide the best copolymer composition curve to represent the experimental data, this curve was drawn in Figure 4.

From these reactivity ratios and the Q, e values for vinylidene chloride ($Q = 0.22$, $e = 0.36$),[6] the Q, e values for 4-cyclopentene-1,3-dione were calculated ($Q = 0.13$, $e = 1.37$). The good agreement between these values and those reported earlier from copolymerizations with methyl methacrylate and acrylonitrile[1] supports the reactivity ratio assignments.

DISCUSSION

The copolymerization of 4-cyclopentene-1,3-dione with p-chlorostyrene appears to be a typical alternating system, as evidenced by the composition curve of Figure 1. The copolymer equation was readily solved by the several methods and gave a unique pair of reactivity ratios, which described a composition curve closely following the experimental values over the entire range. These results thus fail to confirm the behavior of the styrene system, which approached 0.4 mole fraction styrene, and for which a unique pair of reactivity ratios could not be found.[2] If the polymerization involves a charge transfer complex, the p-chlorostyrene would be less able to donate an electron in such a situation than styrene and hence the different results obtained may represent a real difference in the polymerization mechanism. On the other hand, since different analytical techniques were used for the two systems, a determinate error could account for the apparent disparity in the results. Since the carbon analysis for the styrene–dione system would not be as accurate a measure of the copolymer composition as the chlorine analysis in the present case, error in the styrene copolymers is more probable. The question is still open, however. To provide a definite conclusion concerning the nature of these polymerizations, similar systems should be investigated to find other cases of unusual behavior. One such case appears to be the styrene–fumaronitrile system of Fordyce and Ham[7] which also approached a 0.4 mole fraction composition of the copolymers.

In copolymerization with vinylidene chloride, the dione exhibited the typical low reactivity associated with the cyclic monomers in general, which is consistent with the earlier results of copolymerization with methyl methacrylate and acrylonitrile. The Q, e values for the dione as reported

here agree closely with those reported earlier[1] and thus confirm the original interpretation that, in comparison with maleic anhydride and N-butylmaleimide, the dione is of somewhat lower reactivity and has less polarity associated with the double bond system. In comparison with maleimide ($Q = 0.41$, $e = 1.33$),[8] the dione is a less reactive monomer as evidenced from its lower Q value but has about the same polarity as indicated by the closeness of the e values.

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Résumé

La copolymérisation de la 4-cyclopentène-1,3-dione (M_2) avec le p-chlorostyrène et le chlorure de vinylidène a été rapportée. Les copolymères ont été préparés dans des tubes scellés sous atmosphère d'azote avec comme initiateur l'asobisisobutyronitrile. Les bandes d'absorption d'infrarouge à 1580 cm^{-1} révélaient la présence de dicétone-β fortement énolique et indiquaient que la copolymérisation avait eu lieu. Les compositions des copolymères étaient déterminées au départ d'analyses de chlore et les rapports de réactivité ont été évalués. La copolymérisation avec le p-chlorostyrène (M_1) était hautement alternante et fournissait les rapports de réactivité $r_1 = 0.32 \pm 0.06$; $r_2 = 0.02 \pm 0.01$. La copolymérisation avec le chlorure de vinylidène (M_1) fournissait les rapports de réactivité $r_1 = 2.4 \pm 0.6$, $r_2 = 0.15 \pm 0.05$. Les valeurs Q et e pour la dione ($Q = 0.13$, $e = 1.37$), telles qu'elles étaient évaluées au départ des résultats dans le cas du chlorure de vinylidène sont en bon accord avec les résultats rapportès antérieurement pour la copolymérisation avec le méthacrylate de méthyle et l'acrylonitrile et confirment la réactivité généralement basse de la 4-cyclopentadiène-1,3-dione dans des systèmes non-alternants.

Zusammenfassung

Die Copolymerisation von 4-Cyclopenten-1,3-dion (M_2) mit p-Chlorstyrol und Vinylidenchlorid wurde untersucht. Die Copolymeren wurden in zugeschmolzenen Gefässen unter Stickstoff mit Azobisisobutyronitril als Starter dargestellt. Infrarotabsorptionsbanden bei 1580 cm^{-1} liessen das Vorhandensein eines start enolischen β-Diketons erkennen und zeigten, dass Copolymerisation eingetreten war. Die Copolymerzusammensetzung wurde durch Chloranalysen bestimmt und die Reaktivitätsverhältnisse ermittelt. Die Copolymerisation mit p-Chlorstyrol (M_1) besass ausgeprägt alternierenden Charakter und lieferte die Reaktivitätsverhältnisse $r_1 = 0,32 \pm 0,06$, $r_2 = 0,02 \pm 0,01$. Die

Copolymerisation mit Vinylidenchlorid (M_1) ergab die Reaktivitätsverhältnisse r_1 = 2,4 ± 0,6, r_2 = 0,15 ± 0,05. Die aus den Vinylidenchloriddaten berechneten Q- und e-Werte für das Dion (Q = 0,13, e = 1,37) stimmen eng mit den früher bei der Copolymerisation mit Methylmethacrylat und Acrylnitril erhaltenen Werten überein und bestätigen die allgemein niedrige Reaktivität von 4-Cyclopenten-1,3-dion in nicht-alternierenden Systemen.