TABLE IX
REACTIVITY RATIOS OF METHYL ACRYLATE–STYRENE, METHYL ACRYLATE–VINYL ACETATE, METHYL METHACRYLATE–STYRENE, AND METHYL METHACRYLATE–VINYL ACETATE

M_1	M_2	r_1	r_2
Methyl acrylate	Styrene[a]	0.18 ± 0.02	0.75 ± 0.07
Methyl acrylate	Vinyl acetate[b]	9.00 ± 2.50	0.10 ± 0.10
Methyl methacrylate	Styrene[a]	0.460 ± 0.026	0.520 ± 0.026
Methyl methacrylate	Vinyl acetate[c]	20.0 ± 3.0	0.015

[a] F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs, and F. R. Mayo, *J. Amer. Chem. Soc.*, **70**, 1519 (1948). [b] F. R. Mayo, F. K. Lewis, and C. Walling, *ibid.*, **70**, 1529 (1948). [c] F. R. Mayo, C. Walling, F. M. Lewis, and W. F. Hulse, *ibid.*, **70**, 1523 (1948).

tions and the resulting copolymer compositions are given in Tables II–VII. The relative reactivity ratios are summarized in Table VIII and compared with those of FMA and FMMA. Table IX lists relative reactivity ratios for methyl acrylate and methyl methacrylate for comparison with the reactivity ratios of FEA and FEMA.

A close examination of the relative reactivity ratios summarized in Table VIII clearly demonstrates FEA and FEMA are more reactive monomers than FMA and FMMA. When copolymerized with a common comonomer, FEA always has the larger value of r_1 and a smaller value of r_2. Thus, FEA· (FEMA·) adds more readily to FEA (FEMA), in comparison to its addition to M_2, than does FMA or FMMA. Also M_2· adds more readily to FEA (FEMA) relative to M_2 than it does to FMA or FMMA. By including the extra methylene group between the ferrocene and acrylate functions the copolymerizability has been increased. In fact, FEA appears somewhat more reactive than methyl acrylate, while methyl methacrylate seems somewhat more reactive than FEMA (see Table IX). Clearly, FEA and FEMA are suitable acrylate monomers for a wide range of copolymerizations.

Figures 1–3 show the experimental composition–conversion data obtained in FEA–vinyl acetate, FEMA–vinyl acetate, and FEMA–methyl methacrylate copolymerizations. In addition, the theoretical composition–conversion curve for the values of r_1 and r_2 listed in Table VIII is included in these figures to illustrate the fit given by the "best" r_1, r_2 values with the experimental results. It is significant that the r_1, r_2 values chosen gave good fits of the composition–conversion data at both M_1^0/M_2^0 ratios used.

An evaluation of the properties of copolymers of FEA, FEMA, FMA, and FMMA, as well as extended studies of the scope of their copolymerization behavior are in progress and will be reported later.

Acknowledgments. This work was supported by Petroleum Research Fund Grant No. 4479 AC 1-3 and by a Research Corporation Equipment Grant. Further support was provided by a Paint Research Institute Fellowship. The College work–study program provided support for W. Jones. We gratefully acknowledge these sources of support.

Organometallic Polymers. XIII. Addition Polymerization and Copolymerization of π-(Benzyl acrylate)chromium Tricarbonyl

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ABSTRACT: A novel metal carbonyl containing monomer, π-(benzyl acrylate)chromium tricarbonyl (BAC), has been synthesized and both homopolymerized and copolymerized using azobisisobutyrontrile (AIBN) initiation in solution. The reaction of chromium hexacarbonyl with benzyl alcohol gave π-(benzyl alcohol)chromium tricarbonyl which was esterified using acrylyl chloride in ether–pyridine. BAC is the first well-defined monomer of the chromium carbonyls which has been polymerized. Soluble homopolymers having $\bar{M}_n$ as high as 60,000 were prepared and the values of K and a in the Mark–Houwink equation, $[\eta] = KM^a$, were $K = 3.95 \times 10^{-3}$, $a = 0.82$ when $M = \bar{M}_n$. The relative reactivity ratios of BAC (M_1) copolymerizations with styrene ($r_1 = 0.10$, $r_2 = 0.34$) and methyl acrylate ($r_1 = 0.56$, $r_2 = 0.63$) were obtained, and the copolymers were demonstrated to be homogeneous by gel permeation chromatography. From gel permeation chromatography studies a Q factor of 94 was assigned to BAC. Kinetic studies of BAC homopolymerization by dilatometry were not successful because bubble formation in the dilatometer occurred at low polymer conversions. BAC was copolymerized with 2-ferrocenylethyl acrylate to give a polyacrylate containing both chromium and iron.

The addition polymerization and copolymerization of transition metal containing monomers has not yet been extensively studied. Several recent reviews of organometallic polymer chemistry attest to this.[4] Furthermore,

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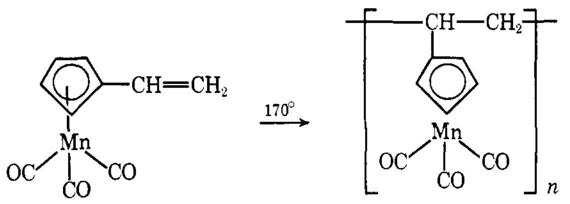
(2) This work constitutes a portion of the Master's Thesis of R. L. Voges, University of Alabama, 1970.

(3) Undergraduate work–study research participant.

(4) C. U. Pittman, Jr., *J. Paint Technol.*, **39**, 585 (1967); H. Valot, *Double Liaison (France)*, **130**, 775 (1966); E. W. Neuse in "Advances in Macromolecular Chemistry," W. M. Pasika, Ed., Academic Press, New York, N. Y., 1968; T. P. Vishnyakova, *Usp. Khim. (USSR)*, **36**, 2136 (1967); E. W. Neuse and H. Rosenberg, *J. Macromol. Sci., Rev. Macromol. Chem.*, **4**, 1, (1970); B. A. Bolto in "Organic Semiconducting Polymers," J. E. Eaton, Ed., Marcel Dekker, New York, N. Y., 1968.

organometal carbonyl polymers are practically absent from the literature with a few exceptions. Vinylcymantrene, one of these exceptions, has been thermally polymerized (eq 1) in bulk by Cais.[5] This polymerization proceeded easily at 170° to give an orange glassy polymer which softened at about 80°. This polymer was recommended as an additive to liquid and solid fuels as a combustion catalyst. The AIBN-initiated homopolymerization of vinylcymantrene and vinylmethylcymantrene and their copolymerization with vinylferrocene (eq 2), styrene, methyl acrylate, acrylonitrile, vinyl acetate, and maleic anhydride have recently been reported by Pittman, *et al.*[6] In addition, these workers prepared and polymerized 1-cymantrenylethyl acrylate.[6] Berger and Manuel[7] have prepared iron tricarbonyl complexes of preformed polybutadiene. In that study, polybutadiene was refluxed with iron pentacarbonyl causing double bond migrations in the polymer resulting in diene–iron tricarbonyl complex sites along the backbone. The only remaining examples of organometal carbonyl addition polymers are the slow AIBN-initiated homopolymerization of π-(hexa-2,4-dienyl acrylate)iron tricarbonyl (eq 3) and its copolymerization with styrene which are under current investigation in our laboratory.[8]



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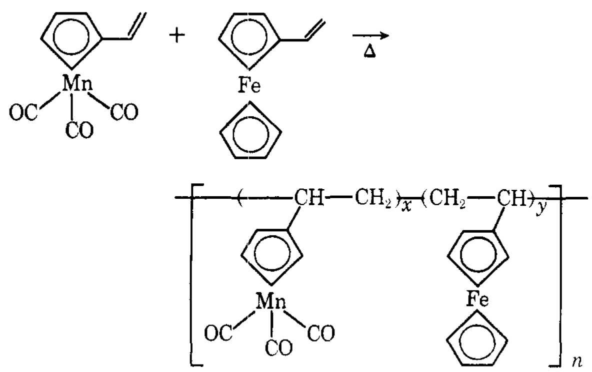

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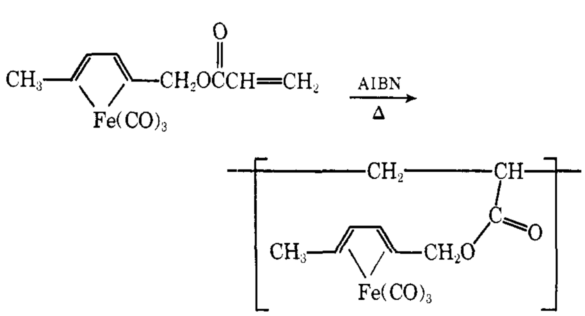
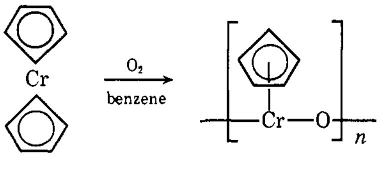


(3)

A few attempts to prepare condensation polymers of organometal carbonyl monomers have appeared. Neuse and Weck[9] attempted to condense cymantrene with aldehydes, but unlike the analogous ferrocene–aldehyde condensations which proceed readily, macromolecular compounds were only obtained under rigorous conditions. Furthermore, these polymers contained less than 20% of the theoretical manganese content. A series of α-hydroxyalkylcymantrenes were polycondensed in both Lewis and proton acids, but substantial metal–ring fission was detected in these processes. This behavior is not unexpected in view of the reduced ability of the cyclopentadienyl ring to undergo facile electrophilic attack when complexed to $-Mn(CO)_3$. No successful reports of addition or condensation polymers of organochromium carbonyl derivatives exist.[10] Fischer, *et al.*,[11] have reported the preparation of a tetrameric chromoxane by the controlled oxidation of chromocene, (π-Cp)$_2$Cr, with molecular oxygen in benzene (eq 4). This tetramer is a blue-violet, highly air- and moisture-sensitive substance with a zero dipole moment. It is postulated to have a puckered eight-membered ring structure.



(4)

The work reported in this paper was undertaken to provide well-defined acrylate derivatives of π-benzenechromium tricarbonyl which could be homopolymerized and readily copolymerized with a variety of commercially important organic monomers. It is part of a larger program in this laboratory to investigate organic polymers which contain transition metals.[12]

Results

Monomer Synthesis. The preparation of π-(benzyl acrylate)chromium tricarbonyl (I) (BAC) is outlined in eq 5. Excess benzyl alcohol was refluxed with chromium hexacarbonyl in a Strohmeier reactor[13] in DME at 140–150° for 6 days. π-(Benzyl alcohol)chromium tricarbonyl was obtained after recrystallization from heptane in 94% yield. This alcohol was then treated with acrylyl chloride at 0° in ether–pyridine under nitrogen. After recrystallization from carbon disulfide, a 52% yield of BAC is obtained as yellow crystals. Attempts to esterify π-(benzyl alcohol)-

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[5] J. Kozikowski and M. Cais, U. S. Patent 3,290,337 (1966); 3,308,141 (1967).

[6] C. U. Pittman, Jr., J. C. Lai, T. D. Rounsefell, J. Chapman, and J. Saad, paper no. 627, 664, 665, and 666, presented at the Joint Southeast–Southwest Regional Meeting of the American Chemical Society, New Orleans, La., Dec 2–4, 1970, see Abstracts of Papers, pp 187 and 199–200.

[7] M. Berger and T. A. Manuel, *J. Polym. Sci., Part A-1*, **4**, 1509 (1966).

[8] Unpublished work of C. U. Pittman, Jr., and O. E. Ayers.

[9] E. W. Neuse and F. J. Weck, manuscript in preparation, reviewed in ref 4e, pp 62–63.

[10] M. D. Rausch, G. A. Moses, E. J. Zaiko, and A. L. Lipman, Jr., *J. Organometal. Chem.*, **23**, 185 (1970).

[11] E. O. Fischer, K. Ulun, and P. Kuzel, *Z. Anorg. Allg. Chem.*, **319**, 253 (1963).

[12] See (a) C. U. Pittman, Jr., *J. Polym. Sci., Part A-1*, **5**, 2927 (1967); (b) C. U. Pittman, Jr., *ibid.*, **6**, 1687 (1968); (c) C. U. Pittman, Jr., *Polym. Lett.*, **6**, 19 (1968); (d) C. U. Pittman, Jr., and J. A. Eikenberry, *J. Alabama Acad. Sci.*, **38** (1968); (e) C. U. Pittman, Jr., J. C. Lai, and D. Vanderpool, *Macromolecules*, **3**, 105 (1970); (f) C. U. Pittman, Jr., J. C. Lai, D. P. Vanderpool, M. Good, and R. Prados, *ibid.*, **3**, 746 (1970); (g) J. C. Lai, T. Rounsefell, and C. U. Pittman, Jr., *ibid.*, **4**, 155 (1971); (h) C. U. Pittman, Jr., R. L. Voges, and W. R. Jones, *ibid.*, **4**, 298 (1971); (i) C. U. Pittman, Jr., R. L. Voges, and J. Elder, *Polym. Lett.*, **9**, 194 (1971); (j) C. U. Pittman, Jr., O. Ayers, S. P. McManus, J. E. Sheats, C. H. Whitten, *Macromolecules*, **4**, 360 (1971).

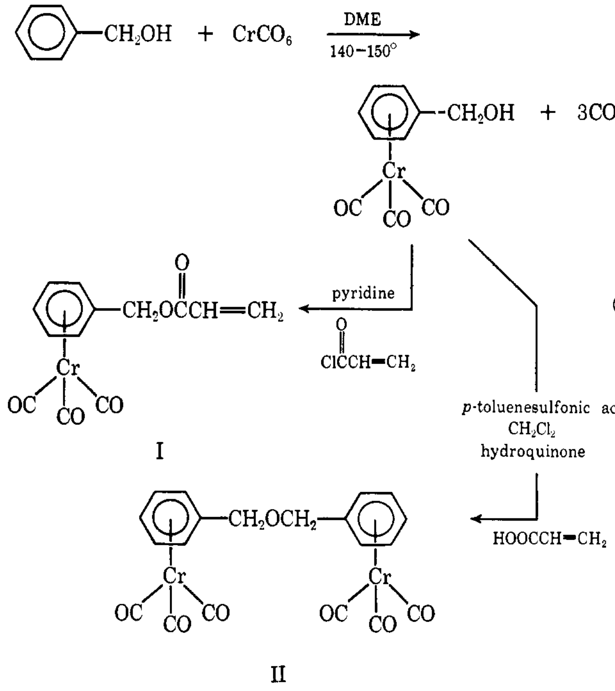
[13] W. Strohmeier, *Chem. Ber.*, **94**, 2490 (1961).

TABLE I
BAC HOMOPOLYMERIZATIONS

Run no.	BAC, g	AIBN, g	Ethyl acetate, ml	Temp, °C	Time, hr	Yield, g	Yield, %	$\bar{M}_n$ in DMF	[η], ml/g in DMF
1	2.000	0.0200	5.0	70	16	1.81	90.5	16,140	11.0
2	1.0000	0.0050	2.5	70	23	0.62	62.0	18,700	13.2
3	1.000	0.0025	2.5	70	78	0.38	38.0	13,800[e]	9.1
4	3.200	0.0320	6.0[a]	70	96	0.84	26.3	7,755[f]	6.1
5[b]	8.216	0.010		70	54	6.11	74.4	39,500	23.2
6	10.000	0.010	20.0	58	360	6.93	69.3	49,000	26.8
7	8.000	0.020	c	60	120	7.20	90.0[d]	60,500	31.0

[a] Polymerized in tetrahydrofuran. [b] Self-initiated polymerization began during storage at −10°. The partially polymerized mass was warmed to 70°; AIBN was added; the mixture was kept at 70° for 54 hr. [c] Melted and polymerized neat, then ethyl acetate added at intervals after the mass thickened. [d] A large amount of insoluble polymer indicates some cross-linking. [e] $\bar{M}_w$ = 20,800. [f] $\bar{M}_w$ = 10.430.

chromium tricarbonyl with methacrylyl chloride were unsuccessful and gave only very low yields of the corresponding methacrylate. Thus, polymerization studies of the methacrylate have not been undertaken.



(5)

Attempts to esterify directly the complexed alcohol with acrylic acid using *p*-toluenesulfonic acid catalyst were unsuccessful. Instead of obtaining BAC, high yields of di-π-benzylchromium tricarbonyl ether (II) were obtained. The structure of the recrystallized ether was characterized by the pronounced ir bands at 1155 cm^{-1} (CO stretch) and the lack of –OH or ester carbonyl absorption. Elemental analysis was in agreement with structure and the nmr spectrum exhibited only aromatic protons at 5.64 ppm (broad s) and methylene protons at 4.46 ppm (s) in the expected ratio of 5:2. The mass spectrum exhibited a molecular ion peak at *m/e* 470 and peaks at 468, 471, and 472 were present in intensity ratios reflecting the natural isotopic abundances of ^{50}Cr 4.4%, ^{52}Cr 83.7%, ^{53}Cr 9.5%, ^{54}Cr 2.4%, and ^{13}C 1.08%. The fragmentation pattern exhibited the loss of CO units predominantly in groups of three, an intense peak for the tropylium or benzyl cation, and ready cleavage of Cr from the organic portion of the molecule. The most abundant peak, in fact, was that of Cr$^+$ at *m/e* 52. These results parallel the well-studied fragmentation patterns of carbonyl derivatives of chromium[14] and manganese[15] reported by Cais and coworkers. The complete details of these preparations are given in the Experimental Section.

Homopolymerization of BAC. Since BAC and poly(BAC) are not readily soluble in benzene, ethyl acetate and THF were used as polymerization solvents. Benzene has usually been preferred in our previous studies[12] because it has a low chain transfer coefficient. The polymerizations were carried out in degassed solutions using recrystallized AIBN as the initiator, and the results of these polymerizations are summarized in Table I.

The homopolymers of BAC were characterized by elemental analysis, vapor pressure osmometry, viscosity measurements, gel permeation chromatography, and infrared spectroscopy. Nmr spectra were obtained, but these were of insufficient resolution and quality to analyze polymer tacticity. BAC homopolymers exhibited ir bands at 3100, 2970–2910, 1975, 1885, 1740, 1460, 1430, 1260, 1165, 1070, 1045, 1018, 998, 815, 750, 660, 628, 531, and 470 cm^{-1}. The carbonyl stretching bands at 1975 and 1885 cm^{-1} of the carbonyl groups attached to chromium were very intense. The ester carbonyl at 1740 cm^{-1} was strong and no trace of the C=C stretch (present at 1625 cm^{-1} in the monomer) was detected. Figure 1 shows the gel permeation chromatogram of BAC polymer 4.

The intrinsic viscosities (Table I) were correlated with

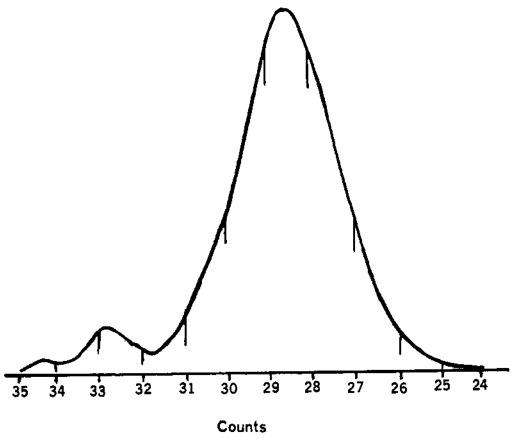


Figure 1. Gel permeation chromatogram of BAC homopolymer no. 1.

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[14] M. Cais, M. S. Lupin, N. Moay, and J. Sharuit, *J. Chem. Soc. A*, 3086 (1968).

[15] N. Moay, A. M. Mandelbaum, and M. Cais, *Tetrahedron Lett.*, 2087 (1965).

TABLE II
COPOLYMERIZATION OF BAC WITH STYRENE AT 60° [a]

Run no.	BAC in feed, g	Styrene in feed, g	AIBN in feed, g	Time, hr	Yield, g	Conversion to copolymer, %	Cr in copolymer, %	Weight fraction in copolymer BAC/sty
1	1.250	1.005	0.0045	21.5	0.988	43.8	11.01	0.603/0.397
2	1.250	1.006	0.0045	8.0	0.296	13.1	10.82	0.675/0.325
3	1.250	1.006	0.0045	35.0	1.725	76.5	10.90	0.581/0.419
4	1.250	1.006	0.0045	15.0	0.575	25.5	11.22	0.608/0.392
5	2.500	0.371	0.0039	14.0	0.845	29.4	13.63	0.765/0.235
6	2.500	0.371	0.0039	29.2	2.076	72.3	12.71	0.865/0.135
7	2.500	0.371	0.0039	27.0	1.952	68.1	13.30	0.812/0.188
8	2.500	0.371	0.0039	17.0	1.069	37.2	13.48	0.772/0.228

[a] Each run used 5 ml of ethyl acetate solvent in the feed.

TABLE III
COPOLYMERIZATION OF BAC WITH METHYL ACRYLATE AT 70° [a]

Run no.	BAC in feed, g	Methyl acrylate in feed, g	Ethyl acetate in feed, ml	Time, hr	Yield, g	Conversion to copolymer, %	Cr in copolymer, %	Weight fraction in copolymer BAC/MA
1	1.250	0.830	5	4	1.018	48.9	11.01	0.633/0.367
2	1.250	0.830	5	8	1.599	76.9	10.82	0.622/0.378
3	1.250	0.830	5	5	1.263	60.7	10.90	0.627/0.373
4	1.250	0.830	5	3	0.527	25.4	11.22	0.645/0.355
5	1.250	0.357	5	15	1.458	80.7	13.63	0.784/0.216
6	1.250	0.357	5	7	1.011	55.9	12.71	0.731/0.269
7	1.250	0.357	4	15	0.259	14.3	13.30	0.765/0.235
8	1.116	0.319	4	5	0.845	46.8	13.48	0.776/0.224

[a] Each run used 0.009 g of AIBN in the feed.

molecular weight *via* the Mark-Houwink equation,[16] $[\eta] = KM^a$. This is expressed as a plot of the log $[\eta]$ *vs.* log $\bar{M}_n$ in Figure 2, and the correlation is surprisingly good considering the plot has been constructed using unfractionated polymers. The values of the constants K and a were 3.95×10^{-3} and 0.82, respectively. The rather large value of a indicates that these polymers are not highly branched, and illustrates that little tendency for the polymer molecules to coil into compact masses exists in highly polar DMF.

BAC homopolymers are pale yellow to orange-yellow solids which can be cast into films. Thermograms were obtained by differential scanning calorimetry. These exhibited little change up to 235° where an endothermic change took place. This endothermic dip maximized at about 245° and by 260° was completed. Beyond 300° the thermograms were erratic. Representative analytical data found for polymers 2 and 5, respectively, were Cr, 17.08, 17.28; C, 51.91, 51.76; H, 4.08, 3.90. Calcd: Cr, 17.44; C, 52.35; H, 3.38.

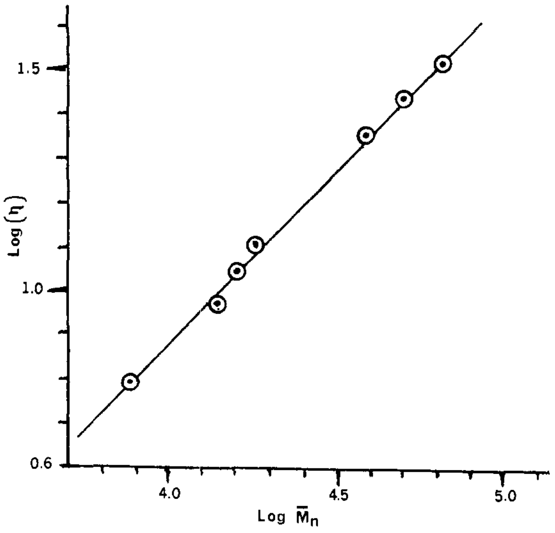
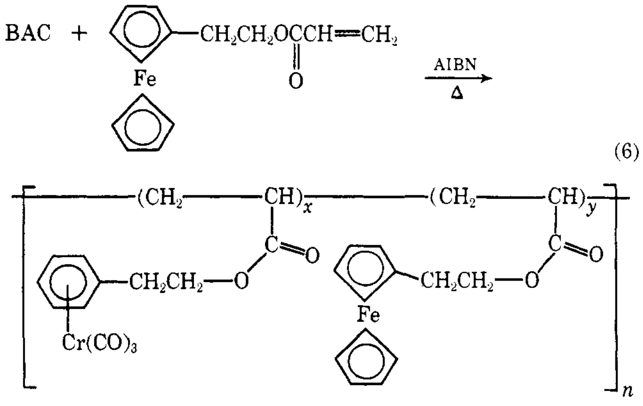


Figure 2. Mark-Houwink plot for BAC homopolymers.

Copolymerization of BAC. BAC was copolymerized with styrene, methyl acrylate, and 2-ferrocenylethyl acrylate[12h] (FEA) in ethyl acetate solutions using AIBN initiation. Copolymerizations with styrene and methyl acrylate were investigated in more detail (see Tables II and III) and the relative reactivity ratios (r_1, r_2) were obtained from these studies. The copolymerization of BAC with FEA is extremely interesting because two transition metals, Fe and Cr, are present in the same polymer (see eq 6). Preliminary ir studies indicate a rather random polymer with both monomers extensively incorporated. In BAC-FEA copolymerizations of equimolar mixtures in ethyl acetate at 65°, yields of 65% after 64 hr were obtained.



(6)

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[16] H. Mark, *Z. Elektrochem.*, **40**, 413 (1934); R. Houwink, *J. Prakt. Chem.*, **157**, 14 (1940).

TABLE IV
RELATIVE REACTIVITY RATIOS FOR BAC AND RELATED COPOLYMERIZATIONS

M_1	M_2	r_1	r_2	Temp, °C	Solvent
BAC	Styrene	0.10 ± 0.02	0.34 ± 0.13	60	Methyl acetate
BAC	Methyl acrylate	0.56 ± 0.11	0.63 ± 0.30	70	Methyl acetate
Methyl acrylate[a]	Styrene	0.18 ± 0.02	0.75 ± 0.07	60	Benzene
FMA[b]	Styrene	0.02 ± 0.01	2.3 ± 0.3	70	Benzene
FMA[b]	Methyl acrylate	0.14 ± 0.02	4.46 ± 0.2	70	Benzene
FEA[c]	Styrene	0.41 ± 0.14	1.06 ± 0.06	70	Benzene
FEA[c]	Methyl acrylate	0.76 ± 0.03	0.69 ± 0.06	60	Benzene

[a] F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs, and F. R. Mayo, *J. Amer. Chem. Soc.*, **70,** 1519 (1948). [b] J. C. Lai, Ph.D. Thesis, University of Alabama, 1970; J. C. Lai, T. D. Rounsefell, and C. U. Pittman, Jr., *Macromolecules*, **4,** 155 (1971). [c] Reference 12h.

The molecular weights of two BAC–styrene copolymers (numbers 3 and 6) were well above 20,000, but more exact figures are not yet available. The copolymer compositions were calculated from elemental analyses and the assumed structure was confirmed by ir spectroscopy which clearly showed bands from both monomers. The key ir bands were observed in the BAC–styrene copolymer at 3100, 2950–2860, 1975, 1885, 1735, 1480, 1440, 1260, 1155, 1070, 1030, 1013, 995, 812, 760, 698, 655, 625, 530, and 470 cm^{-1}; and for poly(BAC–methyl acrylate) at 3100, 2960–2860, 1975, 1885, 1735, 1485, 1440, 1260, 1155, 1070, 1030, 1013, 995, 810, 652, 622, 525, and 563 cm^{-1}. All studies were conducted on copolymers which had been reprecipitated from ethyl acetate into petroleum ether a minimum of three times.

Relative Reactivity Ratios in BAC–Styrene and BAC–Methyl Acrylate Copolymerizations. The relative reactivity ratios were determined by employing the integrated form of the copolymer equation (eq 7) first obtained by Mayo and Lewis.[17] M_1^0 and M_2^0 are the initial molar concentrations

$$\log\frac{M_1}{M_2} = \frac{r_2}{1-r_2}\log\frac{M_1^0/M_2}{M_1^0/M_2} = \frac{1-r_1r_2}{(1-r_2)(1-r_1)} \times \log\frac{(r_1-1)\dfrac{M_2}{M_1}-r_2+1}{(r_1-1)\dfrac{M_2^0}{M_1^0}-r_2-1} \qquad (7)$$

of the two monomers and M_1 and M_2 are their molar concentrations when the polymerization is terminated. A detailed description of the determination of the relative reactivity ratios has previously been described,[18] and the identical procedure was followed in this work.

The relative reactivity ratios determined in this way for the BAC-styrene and BAC-methyl acrylate copolymerizations are summarized in Table IV along with the corresponding ratios for methyl acrylate, ferrocenylmethyl acrylate (FMA), and (FEA) which have been added for purposes of comparison. It is clear upon examination of Table IV that BAC is an active acrylate monomer which is slightly less reactive than both methyl acrylate and FEA but more reactive than FMA. Based on our studies of FMA and FEA, it was concluded that a ferrocene group separated by only one methylene group from the acrylate function exhibits a steric effect which reduces the polymerizability of the acrylate function.[12h] This effect is not operative in BAC. Thus, a π-(benzene)-chromium tricarbonyl group does not sterically retard acrylate polymerization to the extent ferrocene does.

Figure 3 shows the experimental points determined on the composition conversion curves at both initial monomer ratios for BAC–methyl acrylate copolymerizations. The solid lines represent the computer-regenerated composition–conversion curve obtained when the values of r_1 and r_2 listed in Table IV are employed. The reasonable fit of the experimental data at both mole ratios indicates the values of r_1 and r_2 are acceptable.

In summary, BAC is a readily polymerized acrylate monomer. Poly(BAC) is the first well-defined high polymer of an organochromium carbonyl compound which has been reported. Its ready copolymerization demonstrates that π-(benzene)chromium tricarbonyl units may now be readily incorporated into addition polymers of a wide variety, and that such polymerizations appear to proceed without the intervention serious side reactions when AIBN is the initiator. The success with BAC has prompted us to expand our polymer studies of π(benzene)chromium tricarbonyl derivatives and to undertake the synthesis and polymerization of analogous molybdenum and tungsten carbonyls.[19]

Experimental Section

Preparation of π-(Benzyl alcohol)chromium Tricarbonyl. Chromium hexacarbonyl, 50 g (0.227 mol), was placed in a Stroh-

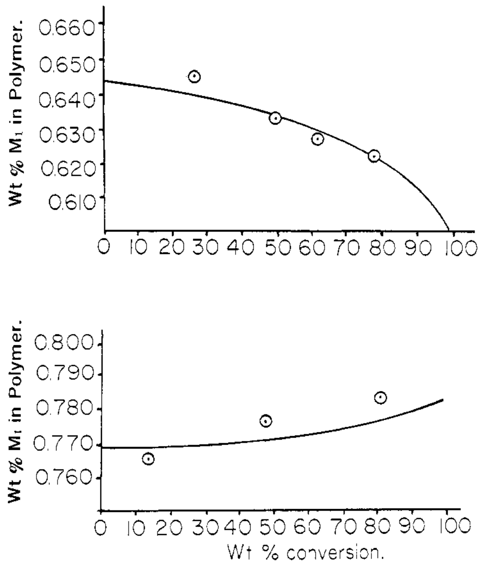

Figure 3. Composition–conversion curve for BAC–methyl acrylate copolymerization: ⊙, experimental points; ——, theoretical curve. Monomer composition of upper curve, M_1/M_2 = 0.606/0.394; lower curve, M_1/M_2 = 0.788/0.222.

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(17) F. R. Mayo and F. M. Lewis, *J. Amer. Chem. Soc.*, **66,** 1594 (1944).

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(19) Research in progress with R. L. Voges, S. P. McManus, G. V. Marlin, and T. D. Rounsefell.

meier[13] reactor under N_2. Benzyl alcohol, 366 g (3.4 mol), was then added. Benzyl alcohol was dried over $CaCl_2$ and distilled before use. 1,2-Dimethoxyethane, 180 g (2.0 mol) distilled from sodium, was then added. 1,2-Dimethoxyethane is an inert solvent which serves to lower the boiling point of the chromium hexacarbonyl–benzyl alcohol mixture. A temperature of 140–150° was maintained in the pot until no white deposits of chroium hexacarbonyl were evident in the condensing portion (Figure 4, part A) of the Strohmeier apparatus (144 hr). By this time almost all of the chromium hexacarbonyl had reacted with the benzyl alcohol turning the color of the solution from colorless to light yellow and finally to dark green-yellow. To isolate the π-(benzyl alcohol)-chromium tricarbonyl, the reaction product was evaporated with a rotary evaporator (100°, 0.1 mm) to dryness. The product was then dissolved in 500 ml of ether, filtered, and washed three times with H_2O–NaCl and distilled water. After drying the ethereal solution over sodium sulfate and filtering, the solution was evaporated to dryness with a rotary evaporator. Recrystallization in heptane afforded 52 g (94%) of π-(benzyl alcohol)chromium tricarbonyl as light yellow crystals: mp 95–96° (lit.[13] 95.5–96.5°); ir (KBr) 3600–3140, 3100, 2960–2880, 1975, 1885, 1460, 1410, 1163, 1152, 1080, 1062, 1052, 1008, 998, 949, 868, 851, 810, 660, 630, 530, 470, cm^{-1}; nmr (CCl_4) δ 5.54 (s, broad, 5, aromatic protons), 2.37 (s, 2, methylene protons), 2.0 (s, 1, OH).

Operating Procedure for the Strohmeier Reactor. At the temperatures necessary for the reactor to be efficient (140–150°), chromium hexacarbonyl sublimes readily with the refluxing solvent vapor and separates above the location at which the solvent condenses. In the Strohmeier reactor, the solvent condenses first in the upper portion of the condenser K_1, and in the lower portion the hexacarbonyl then crystallizes out. In this way the condensed solvent in the condenser K_1 rinses the hexacarbonyl over the "U" tube back into the reaction pot (A). Since the solubility of the hexacarbonyl at room temperature in the condensed solvent is small, most of it would remain in condenser K_1. Therefore, the water temperature in K_1 is kept at a minimum of 60° so that the hot saturated solution flows through the "U" bend back into the reaction vessel. To avoid the possibility that chromium hexacarbonyl might precipitate from the warm saturated solution while going through the "U" bend and plug it up, the water in K_2 is 20–25° higher than the water in K_1. Increasing the diameter of the tubing in the "U" bend is not practical because too much solvent would be out of the reaction pot.

It is advantageous during the heating up of the reactor pot to first turn on cold water in condenser K_1. By this method the hexacarbonyl will be deposited as a tight crust in condenser K_1. After the solvent has started to condense and return to the pot, water of the desired temperature is started in condenser K_1. Over the joint "B," a condenser K_3 is added so that no solvent can escape. Cold water flows through this condenser.

The reactor allows an easy recovery of the unreacted hexacarbonyl in that at the end of the reaction time, cold water is passed through K_1 and any unreacted hexacarbonyl will plate out on the walls of condenser K_1.

Preparation of π-(Benzyl acrylate)chromium Tricarbonyl. Reaction of π-(Benzyl alcohol)chromium Tricarbonyl with Acrylyl Chloride. Pyridine, 7 ml (0.086 mol), was added to a cold (0°) solution of 10 g (0.041 mol) of π-(benzyl alcohol)chromium tricarbonyl in 400 ml of anhydrous ether under nitrogen. Then, 7 ml (0.082 mol) of acrylyl chloride in 4 ml of anhydrous ether was added over a 30-min period. Pyridine hydrochloride precipitated immediately as each drop of acrylyl chloride entered the solution. After a reaction time of 3 hr, during which the temperature of the reaction was gradually allowed to rise to room temperature, the contents was diluted with 400 ml of anhydrous ether and the solution filtered to remove the pyridine hydrochloride. The pyridine hydrochloride was washed with ether until no residual yellow color remained in the ether. The combined ethereal solution was washed five times with 500 ml of $NaHCO_3$–H_2O, NaCl–H_2O, and distilled water. Then the ethereal solution was dried over sodium sulfate and filtered. Rotary evaporation of the solvent left a light tan oil. The oil was dissolved in carbon disulfide and filtered. Recrystallization three times from carbon disulfide yielded 6.21 g (51.4%) of π-(benzyl acrylate)chromium tricarbonyl, mp 51–52°. *Anal.* Calcd: C, 52.35; H, 3.38; C,r 17.44. Found: C, 52.01; H, 3.45; Cr, 17.62. Spectroscopic data included ir (KBr) 3110, 2860–2940, 1975, 1885, 1730, 1665, 1625, 1460, 1410, 1300, 1265, 1178, 1070, 1043, 1008, 980, 801, 650, 620, 525, 427 cm^{-1}; nmr (CCl_4) δ 5.21 (s, 5, aromatic protons), 4.75 (s, 2, CH_2), 5.72–6.49 (ABC pattern, 3, vinyl protons).

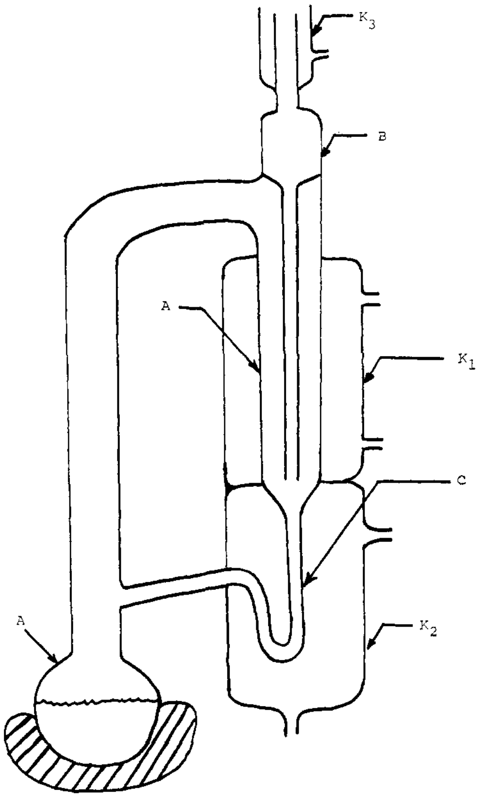

Figure 4. Shrohmeier reactor: A, 1000-ml reaction pot; B, 55/60 mole joint with 24/40 female joint; C, U bend; K_1, condenser no. 1 (input water temperature, 60°); K_2, condenser no. 2 (water temperature, 85°); K_3, condenser no. 3 (cold water).

Preparation of Di-π-benzylchromium Tricarbonyl Ether. To 10 g (0.041 mol) of π-(benzyl alcohol) chromium tricarbonyl in 300 ml of methylene chloride under nitrogen, 0.1 g of hydroquinone, 0.10 g of *p*-toluenesulfonic acid, and 12 g (0.167 mol) of acrylic acid were added. The solution was heated to reflux for 12 hr and cooled. After washing five times with 500 ml of $NaHCO_3$–H_2O and several times with water and drying over Na_2SO_4, the organic layer was concentrated to dryness by rotary evaporation. Recrystallization from 30–60° petroleum ether gave 15 g (78%) of light yellow crystals. This material was identified as di-π-benzylchromium tricarbonyl ether: mp 122–123°; ir 3110, 2980–2870, 1975, 1885, 1460, 1420, 1350, 1220, 1155, 1060, 830, 810, 655, 625, 530, 465 cm^{-1}; nmr (CCl_4) δ 5.64 (s, 5, aromatc protons), 4.46 (s, 2, CH_2); mass spectrum (70 eV) *m/e* (rel intensity) 157 (7.5), 144 (18.2), 143 (7.4), 129 (7.4), 120 (12.7), 91 (22.8), 52 (100).

Polymerization Reactions. The procedures for both homo- and copolymerization reactions were essentially the same.

Polymerization was carried out in either freshly distilled ethyl acetate. Azobisisobutronitrile (AIBN) was used as the free radical initiator. Commercial AIBN was recrystallized three times from methanol before use (mp 102–103° dec). Monomers were stored at −15° in the dark and were freshly prepared before use.

Fischer–Porter aerosol compatability tubes, equipped with valves, were used for polymerization runs. Weighed amounts of monomer, solvent, and initiator were charged to the tubes; the tubes were sealed and degassed at 10^{-3} mm by three alternate freeze–thaw cycles. Liquid nitrogen was used as the freezing medium. After degassing, the tubes were placed in a Haake constant-temperature bath (Model 1280-3, ±0.01°) for a specified time. After removal from the bath, the polymer was precipitated in a rapidly swirling large excess of 30–60° petroleum ether. The polymer solution was diluted with more solvent when necessary so fine particles of polymer precipitated rather than large chunks. This process was repeated three times to ensure that all monomers and other contaminants had been washed from the polymer. After the last precipitation, the polymer was filtered and dried in a vacuum drying oven at 60° for 24 hr and weighed.

Infrared and Nmr Spectra. Infrared spectra were obtained on a Perkin-Elmer Model 237 spectrometer in KBr pellets. Nmr spectra were obtained on a Varian Model HA-100 spectrometer.

Gel Permeation Chromatography. A Waters Associates Model 200 gel permeation chromatograph was used to determine the $\bar{M}_n$, $\bar{M}_w$, and overall molecular weight distributions of the polymers. The polymers were chromatographed in tetrahydrofuran, and the chromatograms were analyzed in the standard fashion advocated by Cazes[20] using points every half-count.[21] The chromatograms were not first corrected for gaussian instrumental spreading as advocated by Tung[22] because this correction is not important in polymers with broad molecular weight distributions, and it only becomes important with increasingly narrow polymer fractions.[22]

As an absolute standard, the values of $\bar{M}_n$ were first determined by vapor pressure osmometry. This value of $\bar{M}_n$ was then used to assign the value of $\bar{M}_n$ at the position in the chromatogram which was the number-average chain length ($\bar{A}_n$). In this way a Q factor was determined, equal to $\bar{M}_n/\bar{A}_n$. Once Q had been obtained on several samples of the polymer, a Q value for that polymer was established as the average of those obtained, and this value was used in calculations of $\bar{M}_w$ and the overall molecular weight distribution. Homopolymers of BAC exhibited a Q of 94.

Viscosity Measurements. Viscosity measurements were made with a Cannon–Ubbelohde semimicro dilution viscometer (50L631) at 30 ± 0.01° and were run in *N,N*-dimethylformamide.

Initial concentrations of polymer were 0.2–0.5 g in 5 ml of solvent, with 5-ml dilutions being made directly into the viscometer Five minutes was sufficient for the contents to reach equilibrium; *i.e.*, subsequent timings differed no more than 0.3 sec. The intrinsic viscosity of the polymer was found by plotting

$$\lim_{C\to 0} \eta\ \mathrm{sp}/C\ vs.\ C$$

(C = concentration of polymer solution in grams per 100 ml of solvent). Table I summarizes the molecular weight and intrinsic viscosity data.

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The Role of Monomer Charge-Transfer Complexes in Free Radical Copolymerization. I. Derivation of Terminal Complex Model Equations[1a]

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ABSTRACT: Copolymerization of monomers through charge-transfer complexes has been investigated qualitatively in the literature. This paper presents a quantitative theory relating deviations of copolymer composition from those predicted by the simple terminal model to the concentration and reactivity of the charge-transfer complexes. Succeeding papers will treat literature examples and show that this approach is an alternate to the penultimate and antepenultimate effect approach.

Compositional deviations from those predicted by terminal polymerization mechanisms[2] have been explained by many authors using penultimate or even antepenultimate models.[3-7] Although these models may rationalize composition quite well, when tested more severely by monomer sequence analysis[8] they frequently predict quite poorly.

A second rationalization of deviations from the simple terminal model was proposed in 1946 for copolymers of maleic anhydride with various monomers.[9] This was the charge-transfer model; electropositive and electronegative monomers can form charge-transfer complexes with each other. When this complex is attacked, both monomers in the complex add as a unit.[10,11] Copolymer compositions tend to be constant.

The model was considered seriously for all copolymerizations but gradually lost favor. Initial attempts to derive copolymer compositions suffered because concepts at that time were not sufficiently advanced. While the concept seemed applicable to some copolymerizations, *e.g.*, maleic anhydride copolymers[9] and styrene–SO_2 copolymers,[10-13] efforts to apply the concept as a mechanism in more conventional polymerizations showed that it was not useful. The

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(1) (a) This paper was presented at the Canadian High Polymer Conference, Aug 1969; (b) this work was performed while J. Seiner was on leave as an Industrial Research Associate at CWRU; (c) PPG Industries; (d) Case Western Reserve University.

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