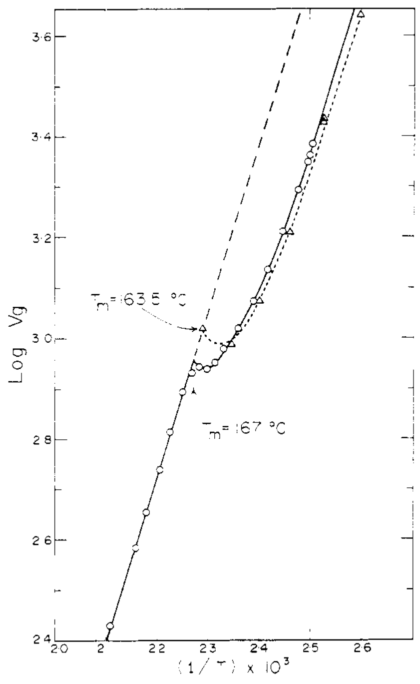


Figure 4. Generalized retention curve for polypropylene using hexadecane probe (column C) O, melting curve, first series; △, melting curve, second series.

those obtained by other procedures is a further corroboration, as is the fact that the values of T_m are not decreased from the expected values for the polymers used. If there were any appreciable solution of the probe molecules in the crystalline regions, some depression of T_m would be anticipated.

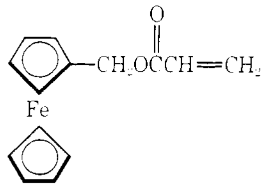
If further experiments verify this conclusion it would appear possible to use this phenomenon to construct a new definition of "order" in polymers. That is, an "ordered region" would be defined as a region impermeable to probe molecules which can permeate the "amorphous regions" of the polymer. The relation of values obtained using this method to those obtained by more conventional techniques using X-ray diffraction or density measurements must await further study in which all three methods are used on identical polymer samples. However it should be pointed out that this new method should in principle be sensitive to the presence of very small crystallites which cannot be detected by standard X-ray diffraction methods. Unlike the density method, the presence of voids or air bubbles should not affect the results either. However it has the disadvantage that the polymer must be in the form of a thin film in order to be studied. In spite of this, the simplicity of the method has much to commend it, and the additional information on thermodynamic interactions and on structural changes such as glass transitions which may be derived from the same data[1,2] represent added features. In view of these considerations we suggest that the "molecular probe" technique will become a standard procedure in the study of melting transitions in macromolecules.

J. E. Guillet and A. N. Stein
Department of Chemistry
University of Toronto
Toronto 5, Canada
Received October 27, 1969

Kinetics of Ferrocenylmethyl Acrylate and Ferrocenylmethyl Methacrylate Polymerization. Preparation of Polymeric Ferricinium Salts

Recently, a large variety of polymers containing ferrocene has been prepared and reviewed.[1] However, acrylate derivatives of ferrocene have not been prepared or polymerized. With the rapidly growing interest in charge-transfer polymers,[2] we felt that ferrocene-containing acrylates might readily be polymerized and subsequently allowed to react with strongly electron-attracting compounds to form polymeric charge-transfer complexes or polymeric ferricinium salts. As in previous studies[3,4] of charge-transfer polymers, we were interested in preparing organic polymers which would exhibit potentially useful conducting and semiconducting properties. Ferrocene has recently been shown to form a charge-transfer complex with tetracyanoethylene[5,6] (TCNE) and to form ferricinium salts with dichlorodicyanoquinone (DDQ) and chloranil.[6] Thus, a similar reactivity in polymeric systems was anticipated. However, initial polymer synthesis might be precluded if the easy oxidation of the ferrocene nucleus leads to preferential reduction of initiator radicals or chain radicals. Iron, as a transition metal, might also catalyze initiator decomposition.

We now report the synthesis of ferrocenylmethyl acrylate (FMA) (I) and ferrocenylmethyl methacrylate (FMMA) (II) and their free radical polymerization in benzene initiated by AIBN. The methiodide salt of N,N-dimethylaminomethylferrocene was converted to hydroxymethylferrocene, mp 81–82° (lit.[7] 81–82°), in 90% yield as reported previously.[7] Esterification of hydroxymethylferrocene in ether–pyridine at 0° with acryloyl chloride or methacrylyl chloride gave FMA



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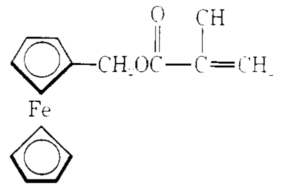

II

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TABLE I
DEPENDENCE OF R_p ON FMA CONCENTRATION IN HOMOPOLYMERIZATION OF FMA IN BENZENE AT 60°[a]

[FMA], mol/l.	$R_p \times 10^6$, mol/l. sec	*R_p/[FMA] × 10^6, $\sec^{-1}$
0.2480	2.021	8.15
0.3076	2.553	8.30
0.4000	3.220	8.05
0.4000	3.357	8.39
0.5046	4.077	8.08
0.5973	4.944	8.28
0.7908	6.478	8.19

[a] [AIBN] = 0.01400 mol/l. for each run.

TABLE II
DEPENDENCE OF R_p ON AIBN CONCENTRATION IN HOMOPOLYMERIZATION OF FMA IN BENZENE AT 60°[a]

[AIBN], mol/l.	$[\text{AIBN}]^{1/2}$	$R_p \times 10^6$, mol/l. sec	$R_p \times 10^5$/ $[\text{AIBN}]^{1/2}$
0.008456	0.09197	2.601	2.83
0.01400	0.1183	3.220	2.72
0.01400	0.1183	3.079	2.84
0.02165	0.1472	4.253	2.89
0.02450	0.1565	4.488	2.87
0.03540	0.1881	5.514	2.93

[a] [FMA] = 0.4000 mol/l. for each run.

TABLE III
DEPENDENCE OF R_p ON FMMA CONCENTRATION IN HOMOPOLYMERIZATION OF FMMA IN BENZENE AT 70°[a]

[FMMA], mol/l.	$R_p \times 10^6$, mol/l. sec	$R_p \times 10^5$/ [FMMA], $\sec^{-1}$
0.2000	2.40	1.20
0.2904	3.47	1.20
0.3998	4.55	1.14
0.3998	4.74	1.19
0.6428	8.26	1.28
0.7983	9.88	1.25
1.0000	13.89	1.39
1.2000	14.50	1.21

[a] [AIBN] = 0.01400 mol/l. for each run.

TABLE IV
DEPENDENCE OF R_p ON AIBN CONCENTRATION IN HOMOPOLYMERIZATION OF FMMA IN BENZENE AT 70°[a]

[AIBN], mol/l.	$[\text{AIBN}]^{1/2}$	$R_p \times 10^6$, mol/l. sec	$R_p \times 10^5$/ $[\text{AIBN}]^{1/2}$
0.005022	0.07086	2.70	3.81
0.01046	0.1023	4.04	3.95
0.01400	0.1183	4.55	3.85
0.01400	0.1183	4.74	4.01
0.01885	0.1373	5.42	3.94
0.02361	0.1537	6.10	3.97

[a] [FMMA] = 0.3998 mol/l. for each run.

(mp 42–43°) and FMMA (mp 52–54°) in yields of 75 and 84%, respectively.[8]

Polymerizations of FMA and FMMA were carried out in degassed benzene solutions[9] in Fisher-Porter aresol tubes, and the kinetics were studied by dilatometry as previously described by Baldwin.[10,11] Polymerizations proceeded smoothly using AIBN[12] as initiator, but attempts to use benzoyl peroxide gave only monomeric ferricinium products. Preparative runs gave pure homopolymers with number average molecular weights ranging from 5 × 10^3 to 20 × 10^3 as measured by gel permeation chromatography (gpc). The values of ΔV/mole were 17.3 ml/mol for FMA and 13.2 ml/mol for FMMA polymerizations in benzene. Kinetic studies, over the first 5–10% polymerization of both FMA (Tables I and II) and FMMA (Tables III and IV) were first order in [monomer] and half-order in [AIBN]. The Arrhenius activation energy of FMA homopolymerization at temperatures between 50 and 70° was 18.7 kcal/mol where [AIBN] = 0.01400 mol/l. and [FMA] = 0.4000 mol/l. The plot of $-\log R_p$ *vs.* 1/°K using the least square method gave a straight line with a slope = 4.088 × 10^3, and $\log R_p = 6.770 - (4.088 \times 10^3)/T$. The activation energy of FMMA homopolymerization between 60 and 75° was 32.7 kcal/mol where [AIBN] = 0.1400 mol/l. and [FMMA] = 0.4000 mol/l. The plot of $-\log R_p$ *vs.* 1/K° gave a straight line with a slope = 7.133 × 10^3, and $\log R_p = 15.43 - (7.133 \times 10^3)/T$. The excellent straight line plots and high reproducibility found throughout the kinetic studies leave little doubt that a classic first-order radical polymerization mechanism adequately describes the mechanism of FMA and FMMA polymerization.

Solution copolymerization of FMA and FMMA with styrene (monomer 2) initiated by AIBN gave a series of homogeneous copolymers (as analyzed by gpc). The relative reactivity ratios were obtained from the copolymer composition equation by the curve fitting method.[13] For FMA–styrene copolymerization r_1 = 0.02 ± 0.01 and r_2 = 2.5 ± 0.1 and using FMMA r_1 = 0.01 = 0.01 and r_2 = 3.6 ± 0.01. Copolymer samples for relative reactivity determinations were obtained by stopping the polymerizations at less than 5% conversion. The monomer ratio in these polymers was obtained unambiguously from elemental analyses (only one monomer contains Fe). At least seven different initial monomer concentration ratios were used in the r_1, r_2 determinations for each monomer pair. The infrared spectra of the copolymers show characteristic monosubstituted phenyl bands at 1601, 1500, 690,

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(8) Satisfactory infrared and nmr spectra and elemental analysis of both FMA and FMMA were obtained. The melting points were obtained by differential scanning calorimetry because thermal polymerization begins to occur measurably at these temperatures. Monomers were easily hydrolyzed in methanol–water systems. Key ir bands for FMA were observed at 3110, 2980–2860, 1720, 1625, 1635, 1460, 1400, 1385, 1280, 1190, 1115, 1050, 994, 955, 937, 820, 740 cm^{-1} and for FMMA at 3108, 2980–2860, 1720, 1640, 1460, 1375, 1302, 1250, 1170, 1114, 1149, 1004, 950, 820 cm^{-1}.

(9) Weighed amounts of monomer, initiator, and benzene (distilled from P_2O_5) were placed in Fisher–Porter tubes and degassed at 10^{-3} mm by three alternate freeze–thaw cycles. After degassing, the tubes were placed in a constant-temperature bath controlled to ±0.01°. FMA and FMMA were prepared shortly before use and stored at −15° in the dark.

(10) M. G. Baldwin, *J. Polym. Sci., Part A-1*, 3209 (1963).

(11) M. G. Baldwin and K. W. Johnson, *ibid., A-1*, 5, 2091 (1967).

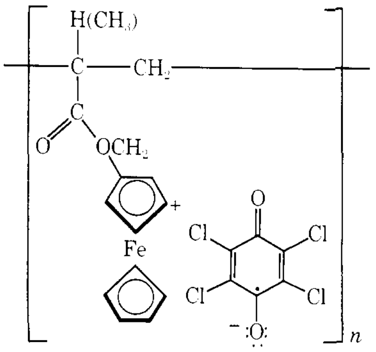
(12) AIBN was recrystallized three times from absolute methanol (mp 102–103° with decomposition) and stored at −15° in the dark.

(13) T. Alfrey, Jr., J. J. Bohrer, and H. Mark, "Copolymerization," Interscience Publishers, New York, N. Y., 1952, pp 8–31.

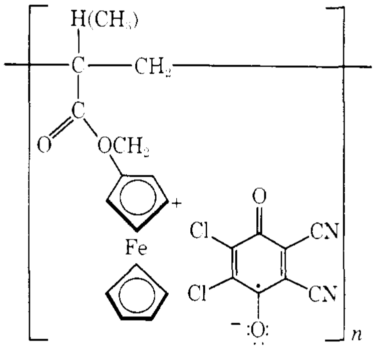
and 748 cm^{-1} and bands characteristic of the ferrocene nucleus at 810, 995, 1104 cm^{-1} as well as the ester carbonyl stretch at 1720 cm^{-1}.

Homo- and copolymers of both FMA and FMMA were dissolved in benzene and treated with benzene solutions of tetracyanoethylene (TCNE), dichlorodicyanoquinone (DDQ), and chloranil. Unlike previous studies with ferrocene,[5,14] charge-transfer derivatives of the polymers with TCNE did not precipitate from solution. Although no long wavelength charge-transfer absorption[5] was observed in the uv spectrum of the benzene solutions, this does not mean that such complexes do not exist in the solid material recovered on aspiration of benzene. Mössbauer studies of the recovered polymer indicate both ferricinium and ferrocene species are present in the solid.[15]

On treatment of the benzene solutions of the FMA and FMMA homopolymers with DDQ or chloranil, black precipitates were immediately formed. Examination of the infrared spectra,[16] elemental analyses, solubilities, and Mössbauer spectra of these precipitates revealed that ferrocene groups had been converted to ferricinium units by electron-transfer to the acceptors.[14,17] The polysalts did not melt at 400° and appeared infusible. The mole ratio of electron acceptor to monomer in these polymeric precipitates varied with the solvent, method of mixing, and mole ratios of starting compounds used. Where elemental analysis indicated the mole ratio of chloranil to ferrocene units in the polysalt precipitates was 1:2, the Mössbauer spectra[6] indicated that 50% of the iron was present in ferricinium groups and 50% in ferrocene groups.[18] Elemental analyses indicated that FMA and FMMA homopolymers could give precipitates with nearly 1:1 monomer–DDQ mole ratios when prepared in benzene solutions. When prepared under identical conditions, the chloranil containing polysalts usually gave a smaller mole ratio. These precipitates were insoluble in nonpolar organic solvents and soluble in DMF. The structure of these polysalts correspond to structures III and IV.



III



IV

Since ferrocene readily forms a green, solid, charge-transfer derivative with TCNE,[5,6,17] it might seem surprising that polymers containing FMA and FMMA do not react cleanly in this manner. However, interaction of the cyclopentadienyl ring's π orbitals with vacant TCNE orbitals is maximized only when these molecules lie in parallel planes (interplanar distance 3.14 Å).[17] Perhaps the weak charge-transfer interaction is sensitive to steric influences of a side chain and to polymer secondary structure.

FMA and FMMA can be polymerized to give normal organic polymers in spite of the presence of an easily oxidizable iron atom in the monomer. The kinetics demonstrate these monomers behave like normal acrylates and they may be compared to benzyl acrylate, recently reported by Patra[19] to undergo first-order polymerization with E_{act}. of 33.1 kcal/mol. The preparation of radiation absorbing acrylate polymers is now possible.[20]

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Charles U. Pittman, Jr.,* John C. Lai
Daniel P. Vanderpool
Department of Chemistry
University of Alabama
University, Alabama 35486

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(14) R. L. Brandon, J. H.. Osiecki, and A. Ottenberg, *J. Org. Chem.*, **31**, 1214 (1966).

(15) Mössbauer studies were performed in cooperation with Dr. Mary Good, Department of Chemistry, Louisiana State University at New Orleans, as part of a larger study now in progress.

(16) The carbonyl stretching frequencies of DDQ (1670 cm^{-1}) and chloranil (1668 cm^{-1}) are shifted to much lower frequencies in the polysalts. In DDQ-poly (FMA) and DDQ-poly (FMMA) the new carbonyl stretch appears at 1575 cm^{-1} in agreement with the shifts found by Brandon, *et al.*, in the corresponding monomeric ferricinium–DDQ complex.[14] The acrylate ester carbonyl stretching frequencies of the polysalts do not shift with respect to their location in the parent uncomplexed polymers (1710–1730 cm^{-1}). That some DDQ might exist in the polysalts in the form of a charge-transfer complex (as opposed to an anion) can not be completely ruled out on examination of the spectra run in fluorolube, Nujol, or KBr on a Perkin-Elmer Model 231 spectrometer.

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(18) Mössbauer spectroscopy easily distinguishes between ferrocene and ferricinium groups. The ferricinium group has a single Mössbauer peak while ferrocene groups exhibit a large quadrapole splitting (~2.4 mm/sec).

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