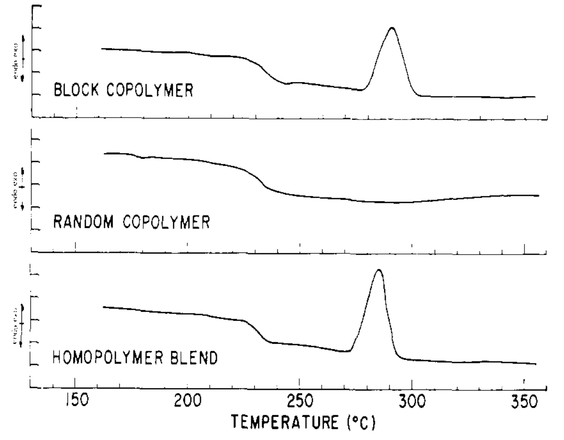

Figure 2. Differential scanning calorimetry traces of dimethylphenol–diphenylphenol copolymers.

mers, while the methyl protons are almost exclusively of the M*M*M type; a small peak at δ 1.86 ppm (P*M*M) presumably corresponds to a juncture between blocks. The absence of dimethylphenol homopolymer is established by the fact that a 20% solution of the copolymer in methylene chloride is stable indefinitely; dimethylphenol homopolymer, even of very low molecular weight, precipitates from methylene chloride as a crystalline polymer–CH_2Cl_2 complex.[6]

Both the random and block copolymers are amorphous as initially obtained and show a single glass transition at 227° (Figure 2). The glass transitions of the homopolymers are too close (225° for dimethylphenol polymer[7] and 230° for diphenylphenol homopolymer[8]) to permit the observation of separate transitions in the block copolymer. Diphenylphenol homopolymer crystallizes when heated above the glass transition and then melts at 480°.[8] The diphenylphenoxy portion of the block copolymer crystallized at 290°, as does the homopolymer, but melting could not be observed because of the onset of decomposition at approximately 450°.

Acknowledgment. The authors are indebted to R. A. Kluge for assistance in the interpretation of dsc and nmr results.

(6) A. Factor, G. E. Heinsohn, and L. H. Vogt, Jr., *J. Polym Sci., Part B*, 7, 205 (1969).
(7) F. E. Karasz and J. M. O'Reilly, *ibid., Part B,* 3, 561 (1965).
(8) A. S. Hay, *Macromolecules,* 2, 107 (1969).

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Study of Crystallinity in Polymers by the Use of "Molecular Probes"

Recent experiments in our laboratories[1,2] have shown that the technique of gas chromatography can be utilized to obtain information about polymer structure and interactions in the solid phase. Although it might appear reasonable to apply the name "gas chromatography of polymers" to such experiments, the terminology is misleading in that the polymer is obviously not in the gas phase, nor is it undergoing a chromatographic separation. The terms glpc (gas–liquid partition chromatography) and gspc (gas–solid partition chromatography) appear to be equally inapplicable. In fact the nature of the experiment has more in common with the molecular beam technique for gas reactions and we prefer therefore to refer to these as studies on polymers using "molecular probes."

In essence, the experiment involves sending a pulse of molecules along a narrow tube which has a thin coating of the polymer to be investigated covering the inner wall or dispersed on an inert support. The probe molecules will undergo random diffusional motion in all directions, upon which is superimposed a velocity U in the forward direction maintained by a flow of inert carrier gas. In general each of the probe molecules will have a velocity component U_p perpendicular to the flow direction which will cause it to impinge on the polymer surface at the wall. If there is no interaction with the polymer there will be no alteration in the component of velocity U_f in the forward direction. On the other hand, any interaction will result in a retardation of the net translational velocity of the probe molecules along the tube direction. The nature of the interaction can be deduced from this change in velocity by application of rather simple theoretical considerations.

In the previous studies[1,2] we showed that the "molecular probe" technique could be used to study glass transitions and thermodynamic interactions in polymer systems. In the present communication we wish to report preliminary studies which indicate that this technique may also represent a powerful new method for studying crystallinity in macromolecules.

The first suggestion that crystallinity in polymers might be studied by gas chromatography is due to Alishoev, Berezkin, and Mel'nikova,[3] who used powdered polyethylene and polypropylene (1%) mechanically mixed in a column of glass beads. Using tetradecane and hexadecene as probe molecules they showed a relatively sharp transition in the retention volume and peak width at a temperature corresponding to the melting point of the polymer. They suggested that the method might be used to estimate the degree of crystallinity in the polymer but gave no further indication of how this could be done. Further they stated that the transition virtually disappeared when the polymer was coated from solution onto the support, which is not confirmed in the present work.

Experimental Section

A Microtek Model DSS-162 gas chromatograph with dual hydrogen flame detectors was modified to include an accurate flow control and pressure gauge on the carrier gas inlet. Oven temperatures were measured to the nearest $^1/_{10}$° using a precision mercury thermometer which was inserted through a 0.25-in. hole drilled through the oven wall. Polyethylene and polypropylene were coated on Chromo-

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(1) O. Smidsrød and J. E. Guillet, *Macromolecules,* 2, 272 (1969).
(2) A. Lavoie and J. E. Guillet, *ibid.,* 2, 443 (1969).

(3) V. R. Alishoev, V. G. Berezkin, and Yu. V. Mel'nikova, *Russ. J. Phys. Chem.,* 39, 105 (1965).

sorb G from hot toluene or xylene solution. The solvent was evaporated while maintaining its temperature above the precipitation temperature of the polymer so that a continuous film would be obtained. The polymer-coated support was packed into $^1/_8$-in. o.d. copper tubing using a mechanical vibrator.

The columns used are shown in Table I.

A uniform flow of nitrogen (~40 cc/min) was maintained through the column and a pulse of probe molecules injected at one end and detected at the other by the hydrogen flame detector. A small pulse of noninteracting gas (methane) was injected with the probe molecules to aid in detection of the carrier gas front. The retention time t_r was determined from the positions of the peak maxima for methane and for the probe molecule at various temperatures. In early experiments with polyethylene (columns A and B), it was demonstrated that there was a negligible change in the retention time for dodecane over a 1000-fold change in sample size (Figure 1). After this, injections of constant size (~10 nl) were used and considered to be equivalent to infinite dilution concentrations.

Materials. Dodecane and hexadecane were Eastman White Label materials used without further purification. Samples of Tenite 800 polyethylene and Tenite polypropylene were obtained by courtesy of the Tennessee Eastman Co., Kingsport, Tenn. The density of the polyethylene as determined by a flotation method was 0.917 g cm^{-3}.

Results and Discussion

As in conventional gas chromatography it is convenient to express the results of these experiments in terms of the retention volume V_r, defined as the volume of carrier gas required to elute the probe molecules. The fundamental quantity from which the various interactions may be deduced is the specific retention volume V_g which is defined by the expression

$$V_g = \frac{273V_r}{Tw} \qquad (1)$$

where T is the temperature of the system (in °K), V_r is the retention volume, corrected for pressure drop along the column,[4] and w is the weight of the polymer film.

The value of V_g for a particular probe molecule (*e.g.*, dodecane) is determined for the polymer at a series of temperatures. The data are plotted in a generalized retention diagram in the form of log V_g as a function of the reciprocal of absolute temperature ($1/T$). Figure 2 shows such a curve for a typical low-density polyethylene (Tenite 800 polyethylene, column B). The data points were obtained in two separate melting experiments on two different days. Two features are immediately noticeable: first, the remarkable linearity of the curve above the melting point, and second the sharp transition at the melting point 109°, corresponding to the complete disappearance of crystallinity. The identity of this point was confirmed by measurements of the melting endotherm of the polymer using a Perkin-Elmer DSC-1B differential scanning calorimeter. At a scan rate of 5°/min, an average of five determinations gave a temperature of 109 ± 0.5° for the disappearance of crystallinity in the polymer.

TABLE I

Column	Length, ft	Polymer	Wt of stationary phase, g	%
A	2	Polyethylene	0.0296	4.10
B	2	Polyethylene	0.0335	4.66
C	2	Polypropylene	0.0377	5.26

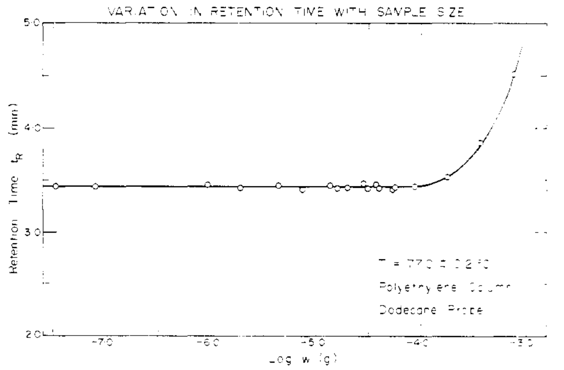

Figure 1. Variation of retention time with sample size for polyethylene (column B) using dodecane as probe molecule, $T = 77.0 \pm 0.2°$.

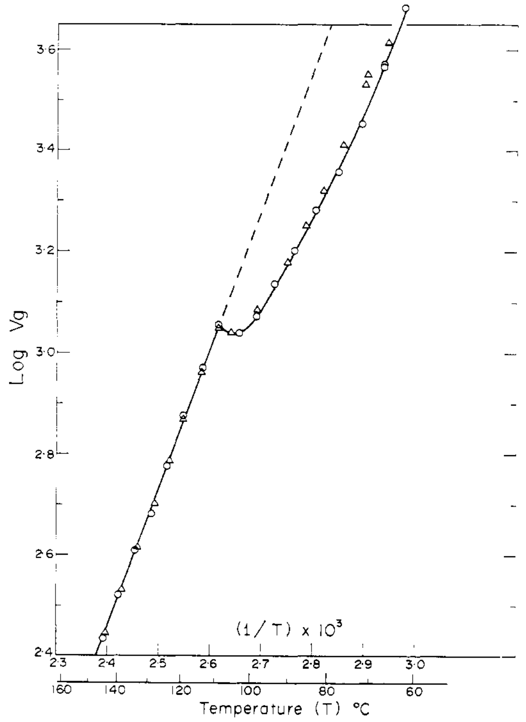

Figure 2. Generalized retention curve for polyethylene using dodecane probe (column B): O, melting curve, first series; △, melting curve, 24 hr later.

The linearity of the curve above the melting point of the polyethylene stationary phase was further confirmed by regression analysis of a least squares fit to the data obtained in three different experiments. The results are summarized in Table II. On the composite of all the data (32 data points) the standard deviation of the slope is 0.56% and intercept 0.03%. The average value of the slope is 2794 ± 16°K. From theoreti-

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(4) S. Dal Nogare and R. S. Juvet, Jr., "Gas-Liquid Chromatography," Interscience Publishers, New York, N. Y., 1962, p 70.

TABLE II
LEAST SQUARES ANALYSIS OF RETENTION DATA ON POLYETHYLENE ABOVE T_m

Series	Slope	Std dev	%	Intercept	Std dev	%	Corr coeff
i	2776.6	20.3	0.73	−4.2073	0.0015	0.04	0.9998
ii	2751.2	12.4	0.45	−4.1449	0.0010	0.02	1.0000
iii	2720.6	73.9	2.72	−4.0496	0.0020	0.05	0.9972
Composite	2794.6	15.7	0.56	−4.2515	0.0011	0.03	0.9996

cal considerations the slope of the log V_g *vs.* $1/T$ relation is given by

$$\text{slope} = \frac{\Delta H_v - (b_1\Delta H_1 + b_2\Delta H_2) - \Delta H_m}{2.303R} \quad (2)$$

where ΔH_v is the enthalpy of vaporization of the probe molecule, ΔH_m is the enthalpy of mixing of the probe molecule and the polymer, ΔH_1 is the enthalpy of adsorption of the probe molecules at the polymer–support interface, ΔH_2 is the enthalpy of adsorption of the probe molecules at the polymer–gas interface, and b_1 and b_2 are constants relating to the contribution of adsorption to the overall retention volume which can be determined experimentally[5] and are related to the surface to volume ratio of the polymer at the two interfaces. At the low concentrations used in these experiments it would seem reasonable to expect that the values of these quantities would approach those of the relevant partial molar quantities. From eq 2 the value of the quantity $(\Delta H_v - (b_1\Delta H_1 + b_2\Delta H_2) - \Delta H_m) = 12.79 \pm 0.07$ kcal mol^{-1}. The linearity of the log V_g *vs.* $1/T$ curve suggests that the enthalpy components of this expression must be nearly independent of temperature over the experimental range above T_m.

If one assumes that the crystalline regions of the polymer are impenetrable to the probe molecules and do not interact with them in any way, then there should be no new enthalpy terms involved in retention at temperatures below T_m. Therefore the slope of the generalized retention plot should not change below T_m. However, since the value of V_g is directly proportional to the weight of absorbing phase, there would be a deviation from linearity if the amount of absorbing phase changed.

In fact then, the extrapolation of the linear portion of the curve to the lower temperature region should represent the theoretical retention curve for the 100% amorphous polymer. The deviation from linearity would then be due to a decrease in the amount of amorphous polymer (corresponding to an increase in the amount of impenetrable crystalline polymer). The amount of amorphous polymer at any temperature below T_m could be estimated by comparing the experimental value of V_g with the theroetical value V_g' obtained from the extrapolated curve at the same temperature. The per cent crystallinity is then given by the expression

$$\%\ \text{crystallinity} = 100\left(1 - \frac{V_g}{V_g'}\right)$$

Using this expression one may determine the degree of crystallinity of the polymer at various temperatures. The values obtained in a typical experiment with Tenite 800 polyethylene are shown in Figure 3. As might be anticipated the values obtained on the melting cycle (*i.e.*, T increasing) are somewhat higher than on a freezing cycle, but the melting points and degrees of crystallinity are similar to the values expected for branched polyethylene of this type. The melting curve is very similar to that reported by Ke[6] for a similar branched polyethylene (Bakelite DYNH) using thermal data obtained on a Perkin-Elmer differential scanning calorimeter. This curve is included in Figure 3 for comparison.

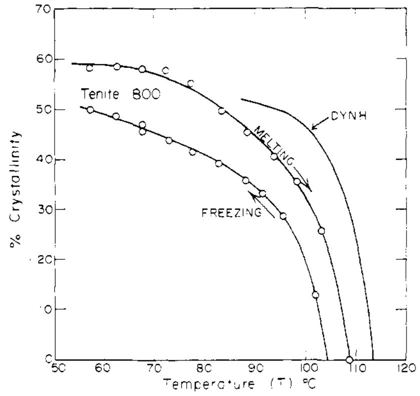

Figure 3. Variation in per cent crystallinity with temperature for Tenite 800 polyethylene, estimated from generalized retention data.

Similar experiments were also carried out using columns containing polypropylene. The experimental retention diagram for polypropylene using hexadecane as the probe molecule is shown in Figure 4. Again a sharp inflection is obtained at $T_m = 165°$. Repeating the temperature cycle on the same column gave a somewhat lower melting point but indicated slightly greater crystallinity. An average of four experiments on the same polymer using the dsc at a scan rate of 5°/min gave a value of T_m of $166 \pm 1°$. In general the values of V_g obtained for polypropylene showed a greater sensitivity to the thermal history of the sample than for the polyethylene. This again is consistent with the known properties of these polymers.

Data were also obtained on polyethylene (column A) using two different probe molecules, decane and dodecane. The curves were quite similar and approximated parallel straight lines in the lower temperature regions, where no further crystallization or melting is taking place during the time scale of the experiment. The values of T_m estimated from the curves also appear to be similar (108–109°).

On the basis of these data we suggest that our original premise regarding the nonpermeability of the crystalline regions to these hydrocarbon probe molecules to be at least a reasonable hypothesis. The general similarity in the melting curves obtained by this method with

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[5] J. R. Conder, D. C. Locke, and J. H. Purnell, *J. Phys. Chem.*, 73, 700 (1969).

[6] B. Ke, *J. Polym. Sci.*, 42, 15 (1960).

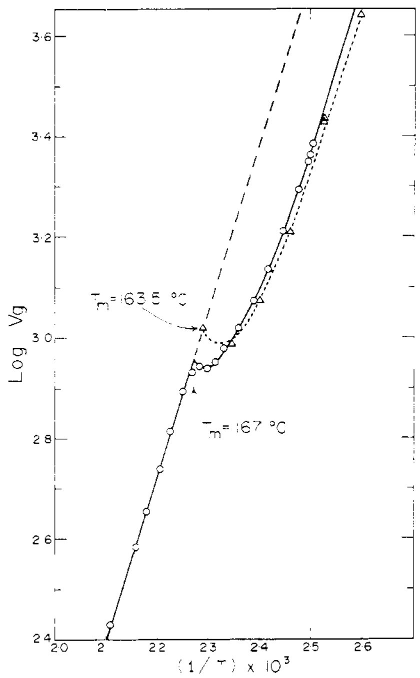

Figure 4. Generalized retention curve for polypropylene using hexadecane probe (column C) ○, melting curve, first series; △, melting curve, second series.

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.

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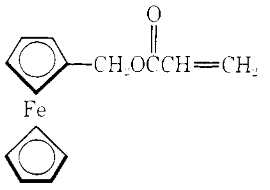
Kinetics of Ferrocenylmethyl Acrylate and Ferrocenylmethyl Methacrylate Polymerization. Preparation of Polymeric Ferricinium Salts

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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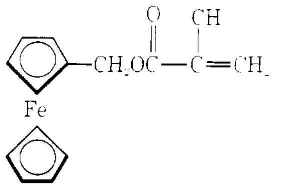

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