Notes

The Application of the Molecular Probe Technique to a Study of Polymer Crystallization Rates

D. G. Gray and J. E. Guillet*

Department of Chemistry, University of Toronto, Toronto, Canada. *Received July 10, 1970*

Most experimental methods for following the changes in crystallinity of polymeric systems have involved measurement of volume changes, changes in absorption spectra, and changes in optical properties.[1] The basis of the novel method reported here is that the bulk interaction between small concentrations of a "probe" molecule and a polymer substrate depends in a simple manner on the degree of crystallinity of the polymer sample. In a recent paper from this laboratory[2] it was suggested that this bulk interaction may be measured by a gas chromatographic method. In this paper, the method is extended to measuring the rate of polymer crystallization; a linear and a branched chain polyethylene were studied using decane as the "molecular probe."

Experimental Section

The experimental data were obtained using an automatic system for sample injection and for measurement of gas chromatographic retention time (Figure 1). The apparatus was based on a Varian Aerograph Model 1720 gas chromatograph equipped with a thermal conductivity detector. Helium was used as a carrier gas. At a preset cycle time, a mixture of nitrogen and decane vapor was introduced into the carrier gas stream using an electropneumatic injection system. The sample size was approximately constant for every injection in a series, and was as small as practicable. (All samples contained less than 1.5×10^{-6} mol of decane; no effect of sample size on retention time was apparent in this range.) The reported results were obtained with two columns. Column A was a 1 m × 0.25 in. o.d. copper tube packed with 0.16 g of high-density polyethylene (Tenite 3310, Tennessee Eastman Co.) coated on 60–80 mesh glass beads. The packing, containing 0.6% by weight of polymer, was sieved 50–80 mesh before use. Column B was 1.2 m × 0.25 in. o.d. copper tubing, containing 30–60 mesh glass beads coated with 0.17 g (0.5% w/w) of low-density polyethylene (Tenite 800, Tennessee Eastman Co.). In both cases the glass beads were coated by stirring with a xylene solution of the polymer at a temperature about 10° below the polymer melting point until the solvent had evaporated.

The net gas chromatographic retention time[3] for decane at a given temperature was measured by feeding the output from the thermal conductivity detector into an electronic peak detection system, which measured the time between the peak maxima for nitrogen (noninteracting) and decane (interacting). The corresponding temperature was measured using an iron–constantan thermocouple attached to the outside of the gas chromatograph column. The net retention time and the temperature were recorded using a digital printer. The carrier gas flow rate, measured using a soap bubble flowmeter, was adjusted to give retention times of from 10 to 500 sec; retention times were reproducible to ±0.2 sec at temperatures above the polymer melting points. It was convenient to use net retention times directly in this work, but these may be readily converted to the more fundamental specific retention volume V_g,[3] using the relationship

$$V_g = t(f/60w)$$

where f = carrier gas flow rate at 0°, corrected for column pressure drop (ml/min); w = weight of polymer in column (grams); t = net retention time (seconds). Experiments to determine the generalized retention diagram were performed at a heating rate of 0.5°/min, using the column oven linear temperature programmer.

The calorimetric data were obtained using a Perkin-Elmer DSC-1B differential scanning calorimeter, calibrated for temperature and power using a sample of indium metal.

Results and Discussion

In order to determine isothermal crystallization kinetics by the molecular probe method, the crystallinity of a polymer sample must first be related to the generalized retention diagram. As in previous work,[2] this diagram, relating the logarithm of net retention times to the reciprocal absolute temperature, showed two distinct regions (Figure 2). As the temperature was increased, the retention time decreased to a minimum, and then increased to a sharp maximum. The shape of this portion of the curve and the position of the sharp maximum were found to depend on the thermal history of the polymer; when the column coating was cooled rapidly from the melt prior to the heating cycle, retention times were longer at a given temperature and the maximum occurred at a lower temperature when compared with a slower annealing process.

At temperatures above the polymer melting point, a straight line relationship was obtained. Using the automatic injection–detection system, the linearity was excellent. In a typical case for 34 data points between 140 and 200°, the standard deviation in the slope was less than 0.2%.

The determination of polymer crystallinity from gas chromatographic retention data rests on the assumption made previously[2] that the probe molecules interact only with the amorphous polymer; the crystalline regions are assumed to be impenetrable. The retention time therefore depends on the amount of amorphous material on the column. By extending the linear portion of a generalized retention curve to lower temperatures, the hypothetical retention time t_a for a totally amorphous sample at any temperature may be obtained. Comparing this with the measured retention time t_m at the same temperature gives the percentage crystallinity using the equation

$$\%\ \text{crystallinity} = 100\left[1 - \frac{t_m}{t_a}\right]$$

Using this relationship, the percentage crystallinity of a sample of linear polyethylene, coated on glass beads was determined as a function of temperature for

---

* To whom correspondence should be addressed.

(1) L. Mandelkern, "Crystallization of Polymers," McGraw-Hill, New York, N. Y., 1964, Chapter 8.

(2) J. E. Guillet and A. N. Stein, *Macromolecules*, 3, 102 (1970).

(3) A. B. Littlewood, "Gas Chromatography," Academic Press, New York, N. Y., 1962.

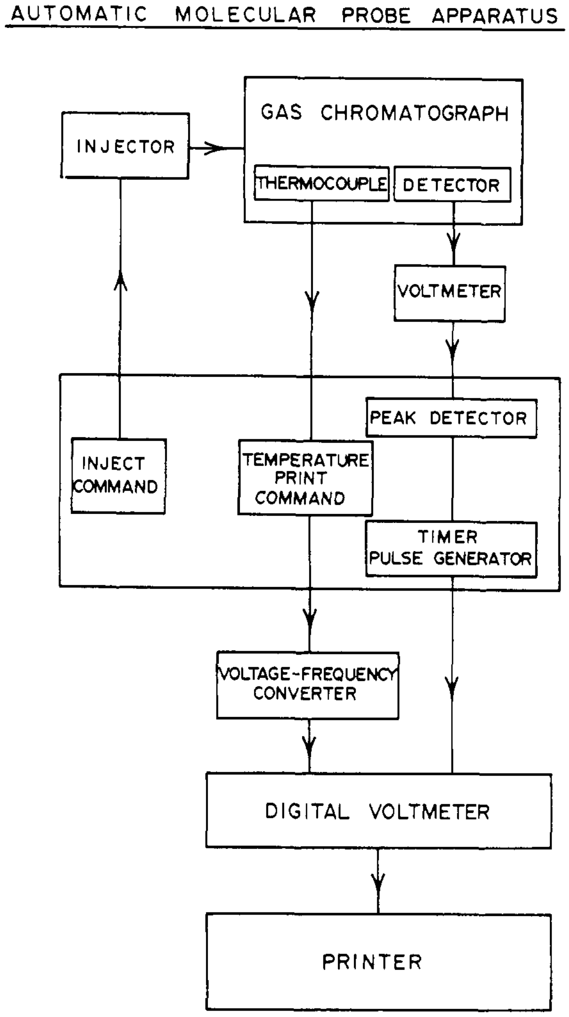

Figure 1. Automatic molecular probe apparatus.

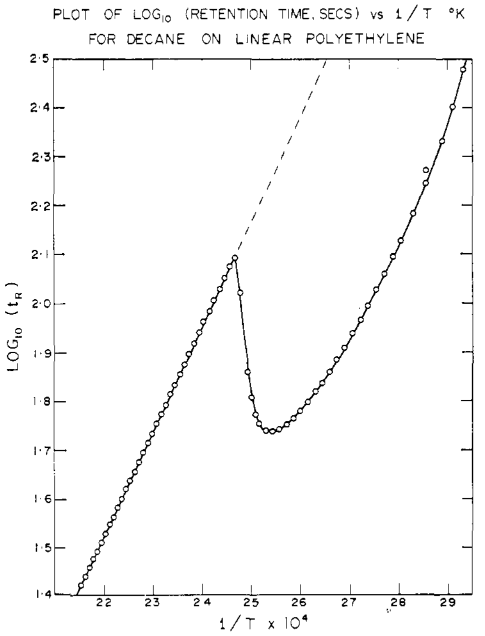

Figure 2. Retention diagram for decane on high-density polyetyhylene. Column A, flow rate 9.3 ml/min corrected to 0°.

two different thermal pretreatments (curves 1 and 2, Figure 3). Rapid cooling of the sample from the melt prior to the measurements lowered the crystallinity and the melting point compared to a sample cooled more slowly.

This effect is to be expected, as the heating rate of 0.5°/min is too fast to allow equilibrium crystallization to be achieved at a given temperature.[4] Consequently the heating curve reflects the morphology of the material, which in turn depends on its thermal history. The fusion of the rapidly cooled material at lower temperatures may be rationalized in terms of its less perfect crystallinity.

Curve 3 on Figure 3 was obtained for comparison using a Perkin-Elmer differential scanning calorimeter to determine the heat of fusion of a sample of the same polyethylene. The sample was subjected to a heating and cooling cycle similar to that used with the gas chromatograph, and its fusion curve was then obtained using the dsc. By integration of this curve, assuming a value of 68.5 cal/g for the latent heat of crystallization of perfectly crystalline polyethylene,[5] the percentage crystallinity of the sample was determined as a function of temperature. The agreement between the calorimetric and the gas chromatographic data is satisfactory; the small difference in the melting curves may possibly result from the fact that in one case the polymer is in the bulk and in the other the polymer is present as a very thin layer on a glass surface. The overall crystallinities are the same within experimental error.

When the polymer on the gas chromatographic column is cooled from the melt to some temperature below the polymer melting point T_m, the retention times for the probe molecule are found to decrease with time. This reflects the decrease in the available amorphous material as crystallization proceeds. The decrease in retention times may be used to follow the crystallization in kinetics. As polyethylene does not form a completely crystalline material, the maximum possible degree of crystallinity must be known to obtain kinetic data in the usual form.

According to our hypothesis, the maximum possible degree of crystallinity at a given temperature is related to gas chromatographic retention times by the equation

$$(\%\ \text{crystallinity})_{\max} = 100\left[1 - \frac{t_e}{t_a}\right]$$

where t_a is the retention time expected for a totally amorphous sample, determined by extrapolation to the temperature under study, and t_e is the retention time for the polymer sample when crystalline and amorphous regions have reached equilibrium. In order to avoid extremely long equilibration times, it was assumed that the pretreatment and heating rate used to obtain curve 2 (Figure 3) gave crystallinities close to the equilibrium values at each temperature. The percentage crystallization of a sample at any fixed flow rate is then given by

(4) L. Mandelkern, "Crystallization of Polymers," McGraw-Hill, New York, N. Y., 1964, Chapter 2.

(5) See ref 4, p 119.

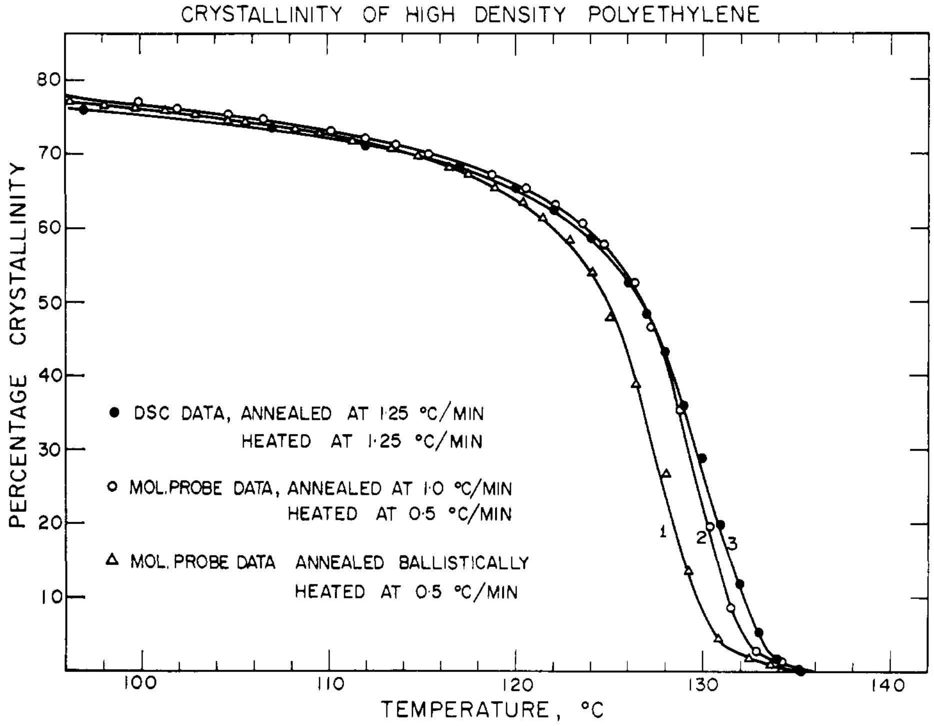

Figure 3. Crystallinity of high density polyethylene; melting curves using molecular probe and calorimetric data.

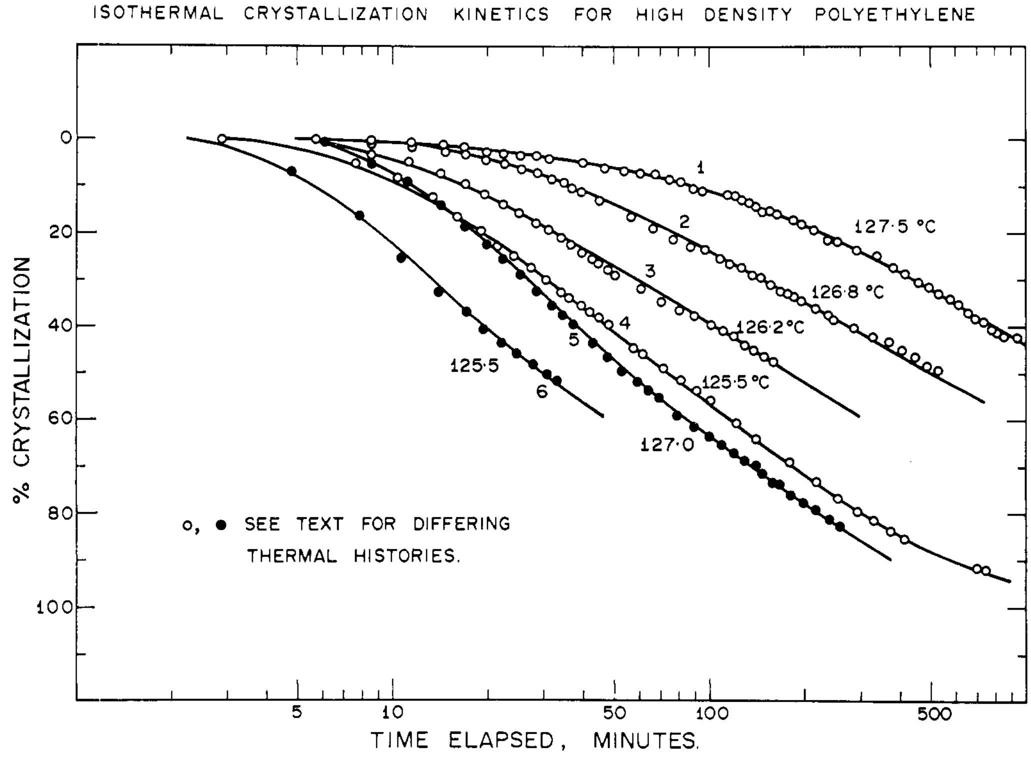

Figure 4. Percentage crystallization as a function of time for high-density polyethylene.

$$100(\%\ \text{crystallinity})/(\%\ \text{crystallinity})_{\max} = \frac{t_a - t_m}{t_a - t_e}(100)$$

Figure 4 illustrates the results obtained for a sample of linear polyethylene using this approach. The general shape of the curves and their positions on the time axis are as expected for linear polyethylenes.[1] However, Avrami plots of the data showed marked curvature suggesting either that the assumptions of the Avrami formulation for crystallization kinetics are invalid in this case or that the nucleation and growth processes change as crystallization proceeds. It seems possible that the physical form of the polymer, as a very thin film coated on glass, may be responsible for

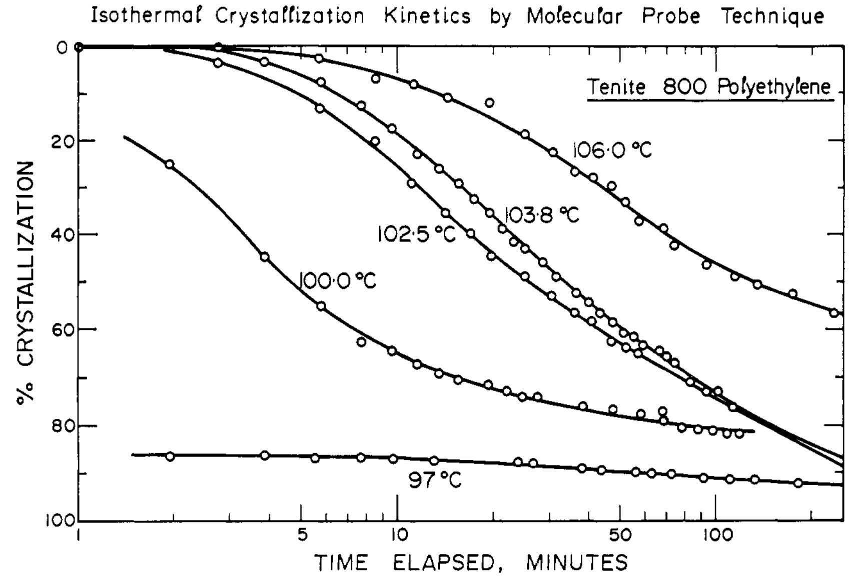

Figure 5. Percentage crystallization as a function of time for low-density polyethylene.

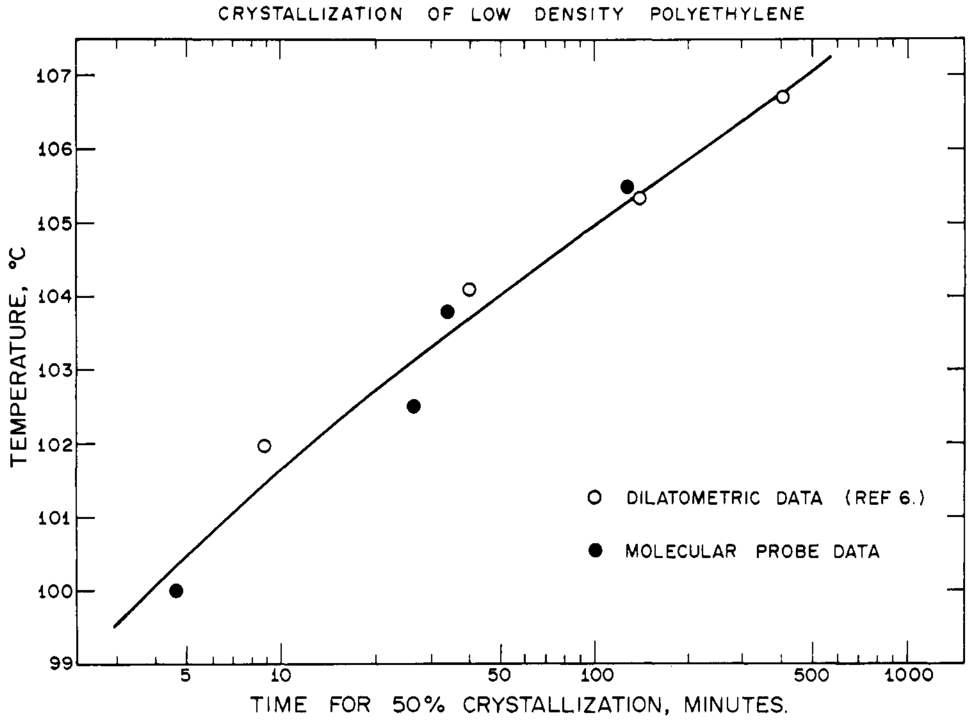

Figure 6. Crystallization half-times for low-density polyethylene.

this behavior; the surface-to-volume ratio has been shown to affect polyethylene crystallization.[6] Surface effects may also be responsible for the effects of pretreatment on the crystallization kinetics illustrated in Figure 4. Curves 1–4 were obtained by preheating the columns to 170° for at least 30 min and cooling quickly to the crystallization temperature. Curves 5 and 6 were heated to 170° for 10 min, then held at 140° for about 30 min before cooling to the crystallization temperature. The onset of crystallization after the latter treatment occurs much more quickly at a given crystallization temperature. This suggests that the glass surface may initiate or stabilize nucleation on sites at temperatures where no crystallinity is detectable.

The results for a branched-chain polyethylene over a range of temperatures are shown in Figure 5. These were obtained using the same method as for the linear polyethylene data. The results are very similar to those obtained previously using dilatometric spectroscopic techniques.[6] The similarity is illustrated in Figure 6, where the experimental time taken to give 50% crystallization is plotted against the crystallization temperature. The results using the molecular probe method correspond reasonably well with those obtained by dilatometric techniques on thin films of the polymer.

These examples show that the molecular probe techniques provides an alternative method for following

---

[6] R. Buchdahl, R. L. Miller, and S. Newman, *J. Polym. Sci.*, **36**, 215 (1959).

polymer crystallization kinetics, giving results similar to conventional methods. No diluent effects[1] were noted, probably because the decane was mixed with the polymer in extremely small amounts and for an insignificant portion of the total crystallization time. Furthermore, crystallinity measurements using different probe molecules and column conditions gave essentially the same crystallinity for a given polymer sample.[7] One useful feature of the method is that retention times may be measured easily to high precision. However, very accurate temperature control and carrier gas flow control are necessary to exploit the method's inherent sensitivity to small changes in crystallinity. Another advantage of this method is that very thin layers of polymer may be studied. (For this work the average coating thickness was less than 10^{-3} cm, assuming that all the glass surface was covered.) The effects of high surface-to-volume ratios and of different types of support surfaces on the rate of polymer crystallization are thus readily measurable.

(7) J. E. Guillet, A. N. Stein, and D. G. Gray, unpublished results.

A Note on Fractionation of Polymers by Thin Layer Chromatography

H. INAGAKI,* F. KAMIYAMA, AND T. YAGI

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan. *Received July 28, 1970*

Application of thin layer chromatography (tlc) to polymer chemistry is widely employed nowadays for various purposes, since Belenkii, and Inagaki, *et al.*, independently reported its utility.[1-4] In the early stage of this study we emphasized it to be advantageous that separation of random copolymer samples by tlc occurred not by difference in molecular weight but solely by that in chemical composition. The reason is quite clear from the thermodynamics of polymer fractionation. In the following period we noticed, however, that this favorable feature of tlc appeared to be limited to the cases in which chromatographic development proceeds according to adsorption and desorption of macromolecules on the substrate.[5] In other words, R_f values (rate of flow) are almost independent of molecular weight so far as the adsorption–desorption mechanism is operative; whereas this is no longer true when precipitation of macromolecules on the chromatoplate takes place—precipitation chromatography. On the basis of this rule we succeeded recently in determining molecular weight distribution of a radically prepared polystyrene by the tlc technique.[6] In the present note we present further experimental evidence supporting the rule mentioned above.

TABLE I
VISCOSITY AVERAGE MOLECULAR WEIGHTS OF SAMPLES[a]

Code	$M \times 10^{-4}$
Isotactic PMMA	
iMA-6	4.3
iMA-4	11.4
iMA-3	16.5
iMA-2	41.2
Polystyrene	
PS-1	0.20
PS-2	0.48
PS-3	1.03
PS-4	5.10
PS-5	16.0
PS-6	49.8

[a] Calculated with viscosity equation $[\eta] = 4.8 \times 10^{-5} M_w^{0.8}$ established for PMMA in chloroform at 25°: J. Bisschoff and V. Desreux, *Bull. Soc. Chim. Belg.*, **61**, 10 (1952).

One piece of evidence was obtained by investigating the development characteristics of a fraction of isotactic poly(methyl methacrylate) (PMMA), coded iMA2, with mixtures of a good solvent and a precipitant toward PMMA, namely chloroform and methanol, respectively. The polymer sample had a molecular weight of 4.12×10^5 (see Table I), and its preparation and characterization were described in a previous paper.[4] The tacticity assessed by applying the method of Bovey and Tiers[7] to the 60-MHz nmr data was $i = 1.0$ and $h = s = 0$. Silica gel was used as the stationary phase. The chromatoplate was activated at 110° for 1 hr just before use. Values of R_f were determined at room temperature as a function of the composition of developer mixture. Figure 1 shows a plot of R_f *vs.* v_2, volume fraction of methanol in mixture.

The value of R_f increases rapidly with increasing v_2 in the region of v_2 from 0 to 0.1 (hereafter referred to as region I), and is unity in the region of v_2 between 0.1 and *ca.* 0.6 (region II). In these regions an adsorption–desorption mechanism should be operative.

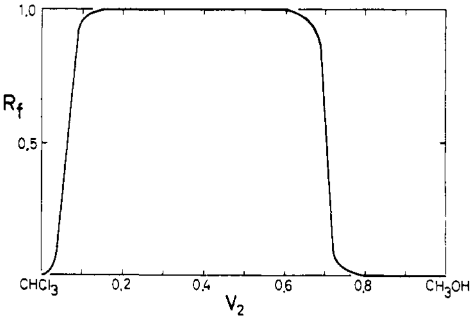

Figure 1. Plot of R_f against composition of developer obtained for a fraction of PMMA, iMA 2, at room temperature.

---

(1) V. G. Belenkii, private communication; V. G. Belenkii and E. S. Gankina, *Dokl. Akad. Nauk SSSR*, **186**, 857 (1969).

(2) H. Inagaki, H. Matsuda, and F. Kamiyama, *Macromolecules*, **1**, 520 (1968).

(3) T. Saegusa, T. Yatsu, S. Miyaji, and H. Fujii, *Polym. J.*, **1**, 7 (1970); A. Yamamoto, T. Shimizu, and S. Ikeda, *ibid.*, **1**, 171 (1970).

(4) T. Miyamoto and H. Inagaki, *Polym. J.* **11**, 46 (1970).

(5) F. Kamiyama and H. Inagaki, Paper No. 18D22, 18th Annual Meeting of the Society of Polymer Science Japan, Kyoto, May 1969; H. Inagaki, *Bull. Inst. Chem. Res., Kyoto Univ.*, **47**, 196 (1969).

(6) F. Kamiyama, H. Matsuda, and H. Inagaki, *Polym. J.*, in press.

(7) F. A. Bovey and G. V. D. Tiers, *J. Polym. Sci.*, **44**, 173 (1960).