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^{-8} 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(7) J. E. Guillet, A. N. Stein, and D. G. Gray, unpublished results.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

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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.

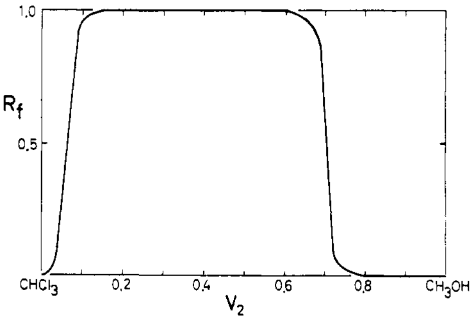

Figure 1. Plot of R_f against composition of developer obtained for a fraction of PMMA, iMA 2, at room temperature.

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(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).

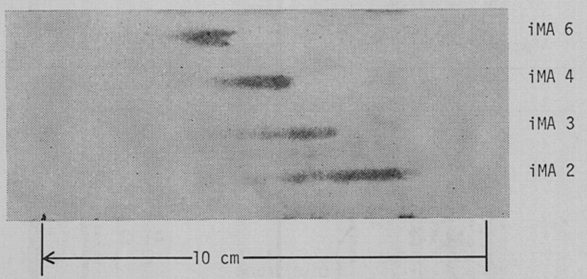

Figure 2. Chromatogram obtained for fractions of PMMA with different molecular weight under a precipitation condition.

When methanol is added to the developer, methanol molecules occupy the adsorption sites on the substrate otherwise for macromolecules. This makes macromolecules mobile so that the R_f becomes higher. In region II, the macromolecules are still soluble in the developer mixture, but methanol molecules occupy all the adsorption sites. As the result the macromolecules are forced to migrate up to the solvent front. However, in the region of $v_2 > 0.6$ (region III), the R_f begins to decrease with further increase of v_2, presumably because the precipitation of macromolecules takes place. A separate experiment showed that when methanol was added at 25° to a 0.8% chloroform solution of this polymer, incipient turbidity appeared first at $v_2 = 0.7$, followed by precipitation of all solutes in the proximity of $v_2 = 0.75$.

The above observation implies that for the chromatographic development of macromolecules, an adsorption–desorption mechanism is responsible in regions I and II, while precipitation is predominantly responsible in region III. Thus we compared the tlc characteristics in regions I and III with respect to the molecular weight dependences of R_f. For this purpose, four fractions of isotactic PMMA having the same tacticity ($i = 1.0$ and $h = s = 0$) but different molecular weight were developed with a chloroform–methanol mixture of $v_2 = 0.05$ on chromatoplate of activated silica gel. Molecular weights of the fractions are listed in Table I. The chromatogram thus obtained indicates practically no molecular weight dependence. In contrast to the development occurring in region I, the chromatogram taken with the mixture having $v_2 = 0.71$ exhibited strong dependency (see Figure 2). These results suggest that the molecular weight dependency of R_f is correlated with polymer precipitation.

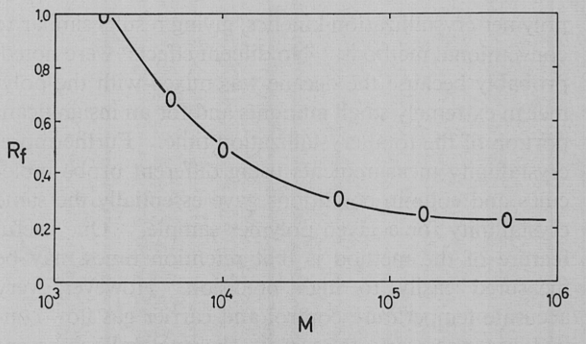

Figure 3. Relation between R_f and logarithm of molecular weight observed by adsorption chromatography for polystyrene fractions.

Another tlc experiment was carried out on six fractions of polystyrene (Pressure Chemical Co., Pittsburgh) with a mixture of cyclohexane (50 ml) and butanone (2 ml) as the initial developer (see Table I). Before the experiment we established that these polymer samples were easily soluble in this mixture at 25° so that no precipitation would take place throughout this tlc experiment. A concentration gradient development was employed: 5 ml of butanone was added to the initial developer at a speed synchronized with the elevation of solvent front. Figure 3 shows the result. It is seen that the molecular weight dependence vanishes rapidly in a range of molecular weights higher than 10^5. This result suggests that the possibility of polymer fractionation based purely on adsorption chromatography is limited to ranges of lower molecular weights. Such a finding is, of course, not new.[8]

In summary, we point out that a complete and effective fractionation of polymers by tlc cannot be achieved so far as the separation mechanism is dominated only by adsorption and desorption processes. It turns out that to separate macromolecules by molecular weight, developers should be chosen so as to give rise to precipitation of macromolecules. This statement differs somewhat from the explanation given recently by Otocka and Hellman for a similar observation.[9]

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(8) See, *e.g.*, K. Bürger, *Z. Anal. Chem.*, **196**, 251, 259 (1963); K. Konishi and S. Yamaguchi, *Anal. Chem.*, **38**, 1755 (1966).

(9) E. P. Otocka and M. Y. Hellman, *Macromolecules*, **3**, 362 (1970).

Communications to the Editor

Laser Raman Studies of Poly(vinyl chloride)

The first reported Raman spectrum of syndiotactic poly(vinyl chloride) was determined by Koenig and Druesedow in 1969.[1] The observed results in Raman agreed well with previous normal coordinate analysis[2] for infrared assignments. Sensitivity of the PVC sample spectrum in ir and Raman to mechanical and thermal history was demonstrated in the ir by Krimm[3] and by the above workers in the Raman spectrum.

Our work on a thermally treated series of purified Diamond 450 PVC has demonstrated a significant difference between the control spectral pattern and those samples which had been carefully heated and cooled

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(1) J. L. Koenig and D. Druesedow, *J. Polym. Sci., Part A-2*, 7, 1075 (1969).

(2) C. G. Opaskar, Ph.D. Thesis, University of Michigan, 1966.

(3) S. Krimm, V. L. Folt, J. S. Shipman, and A. R. Berens, *J. Polym. Sci., Part B*, 2, 1009 (1964).