

## Thin-Layer Chromatographic Separation of Polymers by the Difference in End-Group

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The end-group effect upon polymer separation by thin-layer chromatography (TLC) is examined, using three types of polystyrenes without, and with one and two carboxyl end-groups. TLC experiments by the polarity-controlled adsorption mechanism indicated that complete separation was achieved according to such a slight change in the overall composition of sample as induced by the end-group. On the other hand, it was found that TLC experiments by the solubility-controlled phase-separation mechanism was inappropriate for the purpose.

### INTRODUCTION

Thin-layer chromatography (TLC) has recently been employed successfully to a separation problem of cellulose-styrene graft copolymers obtained by mutual irradiation technique using  $\gamma$ -rays.<sup>1)</sup> The TLC application enabled us to distinguish chromatographically the polystyrene side-chain, grafted on cellulose backbones, from the attendant polystyrene, occluded even after extraction treatment of the graft product. In other words: the polystyrene residue, recovered after complete hydrolysis of the cellulose backbones, was separated by TLC into two components, viz., the one involves some sugar residues at one of the chain ends, while the other does not.

The present work was attempted to reexamine the above finding, namely, the end-group effect upon polymer separation by TLC. For this purpose, anionically prepared polystyrene samples with carboxyl end-groups, which have much more well-defined structure than those recovered from the graft product, were used. Although the present result is confined to polystyrene, we may expect that the basic idea will be applicable to separation of any other types of polymers by the difference in end-group, especially, to the functionality determination of binder prepolymers of industrial interest.<sup>2)</sup>

### EXPERIMENTAL

#### Sample Polymers

Polystyrenes carrying a carboxyl group at one of the chain ends were obtained by anionic polymerization using tetrahydrofuran (THF) and n-butyllithium (n-BuLi), followed by carboxylation of the living polymer. The preparation of polystyryl

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anions was carried out according to our laboratory routine.<sup>3)</sup> The initiator was used in a form of *n*-hexane solution. Carboxylation of terminal styryl carbanions was made with carbon dioxide, which had been purified by passing through a column packed with a system silica gel and calcium chloride in a vacuum system.<sup>4)</sup> Sample polymers thus carboxylated were treated with anhydrous hydrogen chloride to liberate lithium from the polymer chain end. These samples were designated as C-series. On the other hand, an aliquot of the living polymer solution was terminated with a methanol-THF solution, and the polymers thus recovered were designated as M-series.

In this study we also investigated the chromatographic behavior of polystyrenes having a carboxyl group at every chain end. For this purpose we employed our stock samples, which were prepared by radical polymerization of styrene with  $\gamma, \gamma'$ -azo- $(\gamma$ -cyano-*n*-valeric acid) as initiator, and by subsequent fractionation (D-series). The details of preparation and characterization were reported elsewhere.<sup>5)</sup> However, two things should be mentioned for later discussion. The one is that each polymer chain was proved to carry two carboxyl end-groups,<sup>5)</sup> and the other is that each end-group of the D-series samples contains a cyano group in addition to the carboxyl group, as is anticipated from the chemical structure of initiator fragments:  $\text{HOOC}(\text{CH}_2)_2\text{-}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{-(CH}_2\text{)}_3\text{CN}$ . Table I summarizes the characteristic of polymer samples used in this study.

Table I. Characteristics of Polystyrene Samples Employed

Sample code	$M \times 10^{-4a)}$	$M_w/M_n$	No. of COOH per chain
M-1	1.1	1.27	0
C-1			1
M-2	2.0	1.20	0
C-2			1
M-4	3.7	1.30	0
C-4			1
M-5	5.0	1.21	0
C-5			1
D-2	2.3	1.26	2 <sup>b)</sup>
D-4	4.0	1.20	
D-7	7.2	1.14	
D-12	12.0	1.25	
D-32	32.0	1.47	

a) Estimated from maximum peak position in GPC.

b) Each end-group contains a COOH- and CN-residue.

### TLC Technique

The detail of experimental procedures has been described before.<sup>6)</sup> Silica gel, Kieselgel H (E. Merk AG., Darmstadt, West Germany), was used as adsorbent. The thickness of thin layer was adjusted to 0.25 mm. Just before use, the chromato-

plate was activated by heating at 110°C for 1 hr. Stock solutions were prepared by dissolving the sample in chloroform at a concentration of 0.5 g/dl, and spotted on thin layer with a microsyringe. In some experiments, gradient elution technique<sup>6a)</sup> was used. All the experiments were conducted at room temperature (20°C). Reagent grade solvents were used as developer without further purification. Reagent grade chloroform was stabilized with ca. 1% of ethanol.

### GPC Technique

The molecular weight and molecular weight distribution of samples were determined by gel permeation chromatography (GPC). The measurements were carried out at room temperature by using a Shimadzu Gel Permeation Chromatograph Model 1-A. A series arrangement of four columns packed with cross-linked polystyrene gels having upper porosity ratings,  $10^6$ ,  $10^5$ ,  $10^5$ , and  $10^4$ , expressed in molecular weight scale, was employed. The eluent was THF, and the flow rate was adjusted to ca. 1 ml/min.

## RESULTS AND DISCUSSION

### Separation by the Polarity-Controlled Adsorption Mechanism

The present TLC experiment has been so designed that separation takes place according to the difference in chemical composition. This requirement can be fulfilled by making the polarity-controlled adsorption mechanism operative.<sup>7)</sup> To this end, good solvents for polystyrene were used as developer. Three types of samples, M-5, C-5, and D-4, which have different number of end-groups per one chain but similar molecular weights on a level of  $5 \times 10^4$ , were chromatographed with single solvents. The result is summarized in Table II, in which zero and unity in rate of flow ( $R_f$ ) mean that sample remained immobile and migrated up to the solvent front, respectively. From the experimental standpoint it should be noted that this result can be reproduced well only if the silica gel thin-layer is highly activated. We have observed a slight upward tailing in the final spot obtained with benzene for

Table II. Results for TLC Developments with Single Solvents

Developer	$\epsilon^0$ <sup>a)</sup>	Dielectric constant	$R_f$		
			M-5	C-5	D-4
Cyclohexane	0.04	2.02	0	0	0
CCl <sub>4</sub>	0.18	2.22	0	0	0
Toluene	0.29	2.38	1	0 <sup>b)</sup>	0 <sup>b)</sup>
Benzene	0.32	2.28	1	0 <sup>b)</sup>	0 <sup>b)</sup>
CHCl <sub>3</sub>	0.40	4.62	1	1	0 <sup>b)</sup>
THF	0.45	7.42	1	1	1
Acetone	0.56	20.70	0 <sup>n c)</sup>	0 <sup>n</sup>	0 <sup>n</sup>

a) Solvent strength parameter  $\epsilon^0$  values for alumina are relative to the solvent pentane, for which  $\epsilon^0$  is defined equal to zero.<sup>9)</sup>

b) Slightly tailing upward from the starting position.

c) "0<sup>n</sup>" means that  $R_f=0$  because the sample is insoluble in this solvent.

C-5 when we used a chromatoplate which had been left in air for several hours after activation.

As is seen from the table, toluene and benzene allow migration of only the conventional sample (M-5) up to the solvent front, leaving C-5 and D-4 completely immobile on the starting point. While, chloroform enables one to distinguish C-5 from D-4. This finding suggests a possibility of separating a mixture, composed of three polystyrene species without and with one and two polar end-groups, into each component. For such purposes one may employ a stepwise development technique,<sup>8)</sup> which uses benzene (or toluene) and chloroform as developers for the primary and secondary development, respectively.

The above result implies that such a slight change in the overall composition of sample as induced by the end-group can be amplified to the drastic change in the sample migration in TLC, as revealed by  $R_f=0$  and 1. However, the change in chemical composition will exert lesser and lesser influence upon the sample migration with increasing the molecular weight. Thus there should be an upper molecular weight level, beyond which the end-group effect does not more affect the sample migration. Unfortunately we could not estimate the upper molecular weight level, since we failed to prepare C-series samples having higher molecular weights than the present ones. In this connection it should be mentioned that sample D-32, which has a molecular weight of  $3.2 \times 10^5$  and two end-groups per one chain, remained immobile on the starting point after the development using benzene. In this case we must take it into consideration that each end-group attached to D-series samples contains a cyano group in addition to carboxyl group.

In summary: When sample polymers are of low polarities and carry polar end-groups and/or a small number of polar side-groups, TLC separation by the difference in end- and/or side-group is possible by the polarity-controlled adsorption mechanism.<sup>6)</sup> Since such a sample polymer has, as a whole, only a slight affinity to adsorbent, the development should be made by using a "highly active" adsorbent and a "weak" developer. Here "weak" means that the polarity of developer is low.

### **Separation by the Solubility-Controlled Phase-Separation Mechanism**

A supplemental result on the end-group effect upon thermodynamic property of polymer chains will be described below, which is deducible from TLC experiments. The effect has previously been investigated by Ohnuma *et al.*<sup>5)</sup> They found that cyclohexane solutions of polystyrenes carrying carboxyl end-groups, which are identified with the D-series samples, exhibited higher "apparent"  $\theta$ -temperatures<sup>10)</sup> than that for the conventional polystyrene. Therefore, it was expected that such characteristics of the end-group effect might be revealed by TLC experiments according to the solubility-controlled phase-separation mechanism.<sup>6)</sup> In fact, the difference between internal segment densities of linear and star-shaped polystyrene samples has been detected by TLC.<sup>11)</sup>

TLC experiments by the phase-separation mechanism were made for different types of polystyrene samples (see Table I). For the development we selected THF (or chloroform) and acetone as good solvent and nonsolvent, respectively. A gradient elution technique was applied. A mixture of THF (10 ml) and acetone (100 ml),

TLC Separation

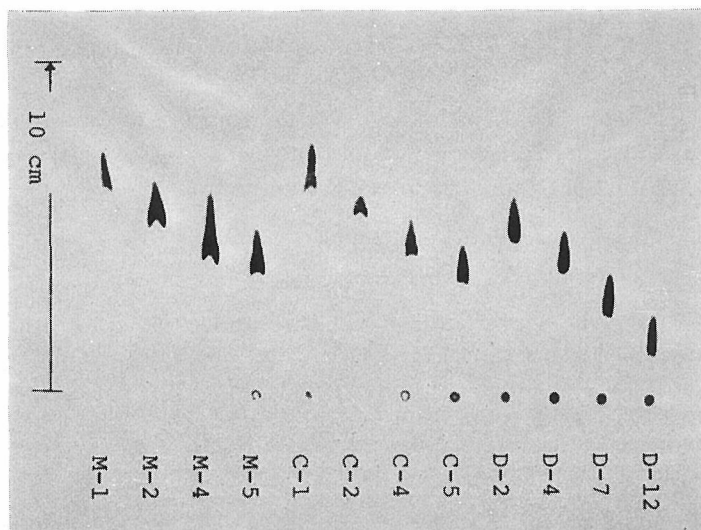


Fig. 1. Chromatogram obtained for three types of polystyrenes with different molecular weight by a THF-acetone elution gradient development.

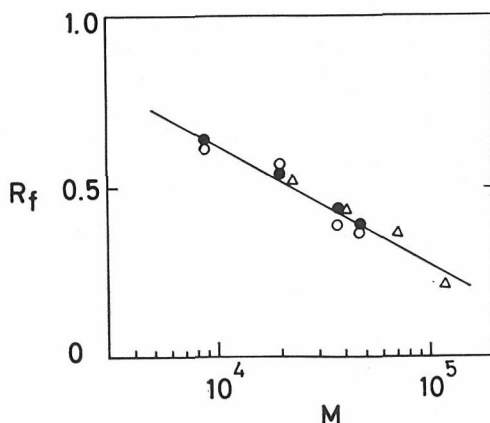


Fig. 2. Plots of  $R_f$  against  $\log$  (molecular weight) obtained for M- (●), C- (○) and D-series (△) by the phase-separation mechanism (refer to Fig. 1).

and THF were used as the initial and adding solvent, respectively. The final composition of developer was 0.17 in volume fraction of THF. A chromatogram thus obtained is shown in Fig. 1, in which one sees distinct molecular-weight dependence found for each series of samples. To compare the dependences, found for each series, the  $R_f$  values were plotted against  $\log$  (molecular weight). As is seen in Fig. 2, all  $R_f$  values for different types of samples fall on a common line without reflecting the difference in end-group. A similar result between  $R_f$  and  $\log M$  was observed by using another developer system chloroform+acetone. From the above results it may be concluded that the end-group effect is not so sensitive upon phase-separation TLC as upon  $\theta$ -temperature determination. Anyway, separation mechanism due to adsorption is quite suitable for polymer separation by the difference in end-group.

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