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Separation of Polybutadiene Depending on Isomeric Stuructures by High Performance Liquid Chromatography

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ABSTRACT: Polybutadiene was separated by isomeric structure using high performance liquid chromatography. With reversed-phase mode using a cross-linked styrene gel as a stationary phase and a mixture of acetonitrile and dichloromethane as an eluent, the polymer was separated by phase separation mechanism. With a cross-linked acrylamide gel and a mixture of hexane and dichloromethane (normal phase), the samples were eluted in order of 1,2 (vinyl), *cis*-1,4, and *trans*-1,4 structure by adsorption mechanism. The resolution by adsorption mechanism was better than one by phase separation mechanism. If acrylonitrile gel was used as stationary phase in the normal phase, samples were adsorbed only weakly to the gel and the resolution was not good.

KEY WORDS Polybutadiene / Isomeric Structure / High Performance Liquid Chromatography / Separation / Adsorption / Phase Separation /

Recently, high performance liquid chromatograhy (HPLC) has been applied to determine the chemical composition distribution of copolymers or to separate steroisomers of poly(methyl methacrylate)s by utilizing solvent gradient from poor or non solvent to a good solvent of the sample.[1-26]

In the previous work we have investigated the separation of styrene-methyl methacrylate copolymers depending on the styrene content using a cross-linked polymer gel as a stationary phase.[27] If both of the mobile and stationary phases were either polar or nonpolar, polymer molecules have had little tendency to adsorb on the stationary phase. If initial eluent was a non-solvent of samples and the solvent gradient of increasing good solvent was applied, the samples were separated mainly by a precipitation-redissolution (phase separation) mechanism. If a polar stationary phase and non-polar and poor solvent were used, samples adsorbed to the stationary phase even when the eluent started to dissolve them. During the solvent gradient of increasing the good solvent content, samples were desorbed and eluted from molecules containing lower amounts of methacrylate units. This combination of mobile and stationary phases is called a normal phase (NP) mode.

On the other hand, in a reversed-phase (RP) mode where a non-polar stationary phase and a polar and poor solvent were used, the opposite elution order was observed, although the separation was done by an adsorption mechanism. It was also found that the adsorption mechanism provided smaller molecular weight dependence and better resolution for the broad molecular weight sample than the phase separation mechanism. In these experiments the polarity of the sample was lower than the gel in case of NP and higher than the gel in case of RP HPLC.

This article describes the separation of polybutadiene depending on isomeric structure using NP and RP HPLC. This polymer is interesting, because it is less polar than gels

normally used for RP column, *e.g.*, polystyrene or poly(octadecyl methacrylate) gels, and also the non-polar eluent used in HPLC is not a poor solvent of it. And also the polarity difference among the samples is very small.

EXPERIMENTAL

Polybutadienes were obtained from Japan Synthetic Rubber Co., Ltd. The characteristics of the samples are listed in Table I. Packing materials for the HPLC columns were prepared by suspension or inverse suspension polymerization as described elsewhere.[23,28] The obtained gels were packed into stainless steel column of 4.5 mm i.d. and 25 cm in length by slurry method.

HPLC was carried out at room temperature (*ca.* 25°C) using two Jasco 880-PU pumps, for providing a good solvent such as dichloromethane, 1-chloropentane, or carbon tetrachloride and the other, poor solvent such as acetonitrile or hexane. The two solvents were mixed together after pumping and were delivered to a Reodyne 7125 injector through a filter. The flow rate was set at 0.5 ml min^{-1} and the proportion of a good solvent was increased linearly in 25 min. A 10 μl portion of dichloromethane solution of the sample (10 mg ml^{-1}) was injected. The column effluent was monitored using an evaporative mass detector (Applied Chromatography Systems Co., Model 750/14) at neblizer gas pressure of 1.4 kg cm^{-2} and at set temperature of 30°C.

Each peak of a mixture was assigned from the elution volume of an individual sample injection.

The cloud point was visually determined by adding a poor solvent into a 1.0 mg ml^{-1} solution of polymer in dichloromethane at 25°C.

RESULTS AND DISCUSSION

Butadiene was polymerized to yield three isomeric units of *cis*-1,4, *trans*-1,4, and 1,2 units depending on the catalyst and other polymerization conditions. Polybutadienes having different isomeric units were separated by RP HPLC using cross-linked styrene or octadecyl methacrylate gel as a stationary phase and a mixture of dichloromethane and acetonitrile as an eluent. As shown in Figure 1a, a mixture of *cis*-1,4 and *trans*-1,4 PBD showed two broad peaks at *ca.* 16 and 22 min, respectively. Figure 1b shows a HPLC curve of polybutadiene having different amount of 1,2 units, which were prepared by butyllithium catalyst. The sample eluted in the order of decreasing amount of 1,2 unit in the elution range from 18 to 23 min. The peaks of 1,2-polyburadienes were narrower than those of 1,4-polybuta-

Table I. Characteristics of polybutadiene

Sample	Isomeric units/%			$\bar{M}_n/10^4$	$\bar{M}_w/10^4$	$\bar{M}_w/\bar{M}_n$
	cis	*trans*	1,2			
trans	7	89	4	5.6	14	2.5
cis	95	2	3	8.0	29	3.6
V-1	41	51	8	25	28	1.1
V-2	25	30	45	20	22	1.1
V-3	7	8	85	25	27	1.1

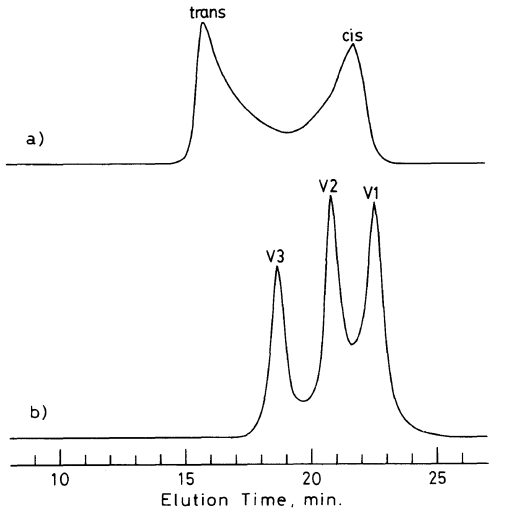

Figure 1. HPLC curves of mixtures of polybutadienes using styrene column and CH_2Cl_2/CH_3CN (30:70 to 100:0) eluent.

Table II. Could point and CH_2Cl_2 content in eluent

Sample	Colud point/%	CH_2Cl_2 content in eluent/%	
		St column	SMA column
trans	69—75	67	69
cis	76—80	75	74
V-1	76—79	75	73
V-2	72—76	71	69
V-3	68—71	67	67

dienes, which may be due to the fact that the former has narrower molecular weight distribution than the latter and to the larger molecular weight dependence of elution volume. As mentioned later, the samples were separated by phase separation mechanism, which usually provides larger molecular weight effect than adsorption mechanism.[19,23,24] Because the two groups of polymers had a similar elution volume range, a mixture of *cis*-1,4, *trans*-1,4, and 1,2-polybutadienes were not well separated.

As shown in Table II, the dichloromethane content at the peak top is almost equal to the cloud point for each polymer, which indicates that the separation was done by the phase separation mechanism. It is noteworthy that the good solvent content of the eluent was independent of the type of the gel, which is characteristic to the phase separation mechanism. In the case of polybutadiene the polarity of the sample is lower than the gel, and no adsorption was observed. On the other hand, in the case of styrene–methyl methacrylate copolymer which is polar than the gel, the same chromatographic system provide the separation due to adsorption mechanism. Therefore, it can be said that polarity of the sample should be higher than the gel by adsorption mechanism in RP HPLC. Therefore, less polar stationary phase than those used in this study is thought to be necessary for the separation by adsorption mechanism.

Separation of isomeric polybutadienes was tried by NP mode using dichloromethane/hexane eluent. When polyacrylonitrile (AN) gel was used as a stationary phase, polymers were eluted at the elution range of 12 to 15 min with the elution order of 1, 2, *cis*, and *trans* isomers. However, when a mixture of the five polymers was injected, only two peaks were observed; one overlapping peak due to 1,2 and *cis*-polymers and the other due to *trans* polymer and shown in Figure 2. The poor resolution of the mixture may be attributed to the weak absorption in this HPLC system. Therefore, it is considered that less polar eluent than hexane is necessary to separate polybutadienes by adsorption mechanism, if AN gel is used as a stationary phase.

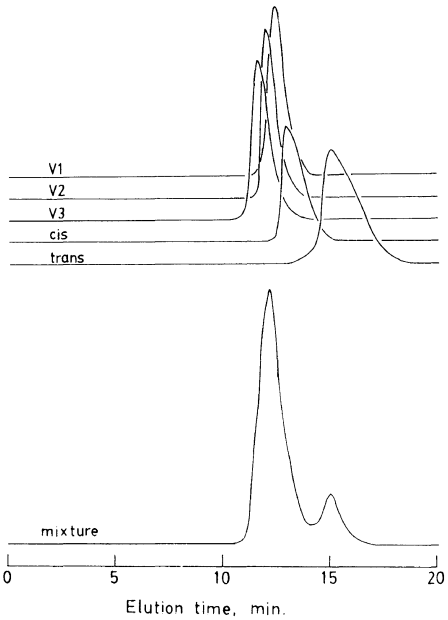

Figure 2. HPLC curves of polybutadienes using acrylonitrile column and CH_2Cl_2/hexane (0 : 100 to 100 : 0) eluent.

It was found that the adsorption became stronger when a more polar gel was used in NP mode.[25,27] Polyacrylamide (AA) gel was found to be more polar than AN gel,[28] since a polymer having a higher solubility parameter (SP) value is generally more polar and the SP value of the former is 13 $cal^{1/2}$ $cm^{-3/2}$ and that of the latter 11 $cal^{1/2}$ $cm^{-3/2}$. AA gel was used instead of AN gel with the same eluent. As

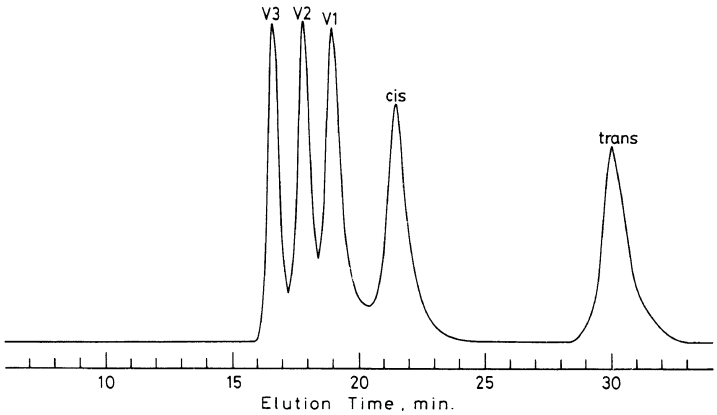

Figure 3. HPLC curve of a mixture of five polybutadienes using acryamide column and CH_2Cl_2/hexane (0:100 to 40:60) eluent.

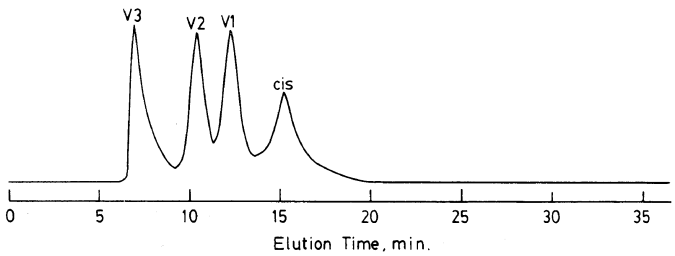

Figure 4. HPLC curve of a mixture of five polybutadienes using acerylamide column and CCl_4/hexane (40:60 to 100:0) eluent. (*trans* polymer did not eluted out.)

shown in Figure 3, the three types of polymers were separated with the elution order of 1,2, *cis*, and *trans*-polybutadienes. This elution order is same as that of butadiene oligomers separated by NP mode using styrene gel column and 2,2,4-trimethylpetane eluent.[29] The peak widths of *cis* and *trans* polymers were narrower compared to RP (Figure 1a). The narrow peaks in NP may arise from the smaller molecular weight effect, which is usually observed for the separation by adsorption mechanism. It is clear that the samples were separated by adsorption mechaism, since the samples were soluble in any composition of hexane and dichloromethane.

When a mixture of carbon tetrachloride/hexane was used as an eluent with AA gel column, only 1,2- and *cis*-polybutadienes were eluted as shown in Figure 4 and *trans* polymer was not eluted, even pure carbon tetrachloride was used as an eluent. The difference of elution behavior of the two types of eluent is attributed to the fact that carbon tetrachloride has lower SP value (8.6) and weaker desorption ability in NP HPLC than dichloromethane (SP=9.3).[30] By using 1-chloropentane/hexane eluent, the same elution order was obtained as one using dichloromethane/hexane eluent (Figure 5). Thus, by using AA column, the elution order did not change by the change of the eluent, although the content of hexane at the peak position differ with the type of solvent.

Inagaki *et al.*[31] separated isomeric polybutadienes by thin layer chromatography (TLC) using silica gel and various types of eluent. In their experiment the developing order using carbon tetrachloride as eluent is 1,2-, *trans*-, and *cis*-polymer, while using 1-chlo-

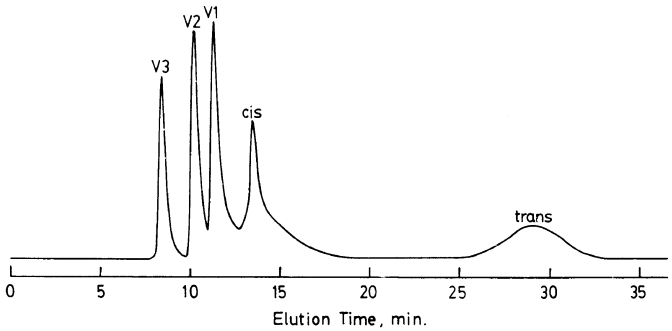

Figure 5. HPLC curve of a mixture of five polybutadienes using acrylamide column and 1-chloropentane/hexane (20:80 to 100:0) eluent.

ropentane 1,2- and *cis*-polymers developed to the solvent front and trans-polymer remained at the starting point. The difference of HPLC and TLC experiments may be due to the difference of the sample concentration in the mobile phase or the special interaction between the sample and silica gel. In the case of separation of poly(methyl methacrylate) by tacticity, similar difference of the elution order is observed among TLC using silica gel and HPLC.[26]

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