Molecular Characterization of Hydroxyl-Terminated Polybutadienes

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Synopsis

A comparative study has been made on the functionality distribution of two hydroxyl-terminated polybutadiene products which are used largely as prepolymers for sealants, adhesives, and solid propellants. They are known to possess nearly the same molecular characteristics. To this end, each product was fractionated into 17 fractions with different molecular weights by the preparative GPC technique. Sample fractions thus obtained were subjected to "polarity-controlled adsorption" thin-layer chromatography (TLC) to determine the functionality distribution. From these experimental results it was concluded that a decisive difference between these products consists in the functionality distribution within a molecular weight range higher than 7000.

INTRODUCTION

It is now well known that when telechelic liquid polybutadienes are used as adhesives, sealants, or binder components of solid propellants, the performance of the final products is closely related not only to the average molecular weight and functionality but also to their distributions. Thus much attention has been focused on the molecular characterization, especially on the determination of functionality distributions.[1-10]

More than 10 years ago adsorption column chromatography (ACC) was first introduced to separate hydroxyl-terminated polybutadienes by the difference in functionality.[1,2] A little later gel permeation chromatography (GPC) furnished with an RI and a UV detector was applied to estimate the average functionality of hydroxyl-terminated polybutadiene fractions eluted at different retention times. Prior to fractionation the hydroxyl-terminated group was made responsive to UV light by modifying it with phenyl isocyanate.[3,4] Data observed by this method were indicative of a trend that the functionality continuously increased with increasing molecular weight for the samples prepared by a radical initiation. However this result was not in agreement with that observed by the ACC method.[2] Very recently, Guise and Smith applied liquid chromatography to oligomeric urethane polyols under a sophisticated condition and succeeded in their rapid separation according to the functionality.[5]

Several years ago, Russian groups and our research group independently demonstrated that thin-layer chromatography (TLC) could be used to estimate functionality distributions of oligomers having different functionalities[6-9] and of telechelic butadiene prepolymers.[10] Especially, our group used "polarity-controlled adsorption" TLC[11] and succeeded in separating

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commercial products of α, ω-polybutadiene–diols and –dicarboxylic acids into the non-, mono-, and difunctional components by discrete smears on the chromatogram.[10] This separation was achieved on the basis that the adsorption force of the sample onto the stationary phase is enhanced by an increase in the functionality when compared on the same molecular weight level. The sample having a higher functionality is more strongly retarded on migration, thus showing a lower R_f (rate of flow).[12]

As will be understood from the above description, our success in the separation was attained because the samples tested were prepared by anionic polymerization; therefore, had narrow molecular weight distributions (MWD). For analyzing samples having broader MWD, it should be reminded that, when compared on the same functionality level, the migration distance, hence the R_f, increases with increased molecular weight.[13] Such a molecular weight dependence of R_f will prominently draw back TLC separation according solely to the difference in functionality.

In this work, molecular characterization with emphasis on the functionality distribution has been made for two commercial products of hydroxyl-terminated polybutadienes which are believed to be prepared by a radical initiation procedure. For the purpose of avoiding the effect of molecular weight upon TLC separation by the difference in functionality, the sample product was, in advance, fractionated into a number of fractions by using a preparative GPC technique. The functionality distribution for each fraction thus recovered was then estimated with the aid of TLC technique. On the basis of data obtained for all fractions, the difference in functionality distribution between these two commercial products will be discussed.

EXPERIMENTAL

Materials. Hydroxyl-terminated polybutadiene samples studied in this work are two commercial products from the Atlantic Richfield Corp., which were designated as R45M and R45HT. These samples and the other chemical reagents were used without further purification.

Fractionation of Samples. A Toyo Soda Model HLC-827 Preparative GPC (Toyo Soda Co., Ltd., Tokyo) furnished with columns of G3000HG6 and G2500HG8 (available from the same company as above) was employed for the fractionation experiment. For each fractionation run, 0.1 g of sample was loaded into the apparatus in a form of 3.3 wt % chloroform solution with 0.05% antioxidant. The elution was made to fractionate the sample into 17 fractions with chloroform containing 0.5% antioxidant at a flow rate of 7.0 mL/min at room temperature. By introducing a microcomputer system (HLC-CP8 Model III, Toyo Soda Co., Ltd.), the same fractionation run was automatically repeated 10 times, and the cumulation of each fraction was made on the basis of a constant time interval.

GPC Experiments. MWDs of the whole samples and each fraction obtained were determined with a Toyo Soda Model HLC-802 Analytical GPC in our laboratory. Tetrahydrofuran (THF) was used as eluent. The calibration curve was constructed by referring to the Mark–Houwink–Sakurada equations for polystyrene and polybutadiene in THF.[14] Its validity was proven by three polybutadiene samples with known number average molecular

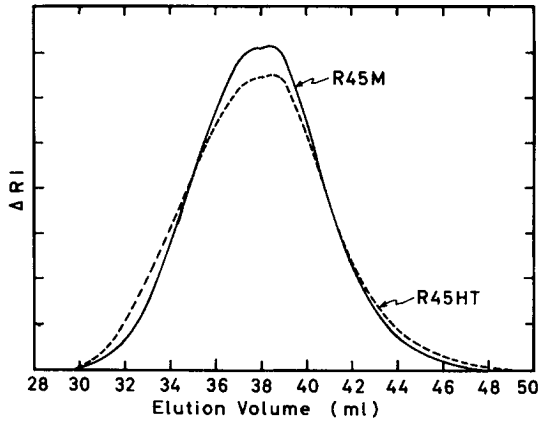

Fig. 1. GPC elution curves of R45M and R45HT.

weights ranging from 2000 to 10,000, estimated by vapor pressure osmometry.

TLC Experiments. Each sample fraction was subjected to TLC to estimate the functionality distribution. Silica gel, Kieselgel 60H (E. Merck, Darmstadt), was used as adsorbent. The preparation of thin-layer and the development were made according to our laboratory procedure.[10,11] Since this series of TLC experiments was aimed at a comparison of the functionality distribution between R45M and R45HT, each development run of sample fractions was conducted with the whole samples so far as possible. The chromatogram was visualized by spraying a solution of thimol blue saturated in equibinary of water and methanol, and then 10 N sulfuric acid. The chromatogram thus visualized was photographed, and the film was subjected to a densitometric scanning for quantitation.[11,15]

RESULTS AND DISCUSSION

Fractionation Results

GPC elution curves observed for the whole samples, R45M and R45HT, are shown in Figure 1, and the average molecular weights computed from GPC data are given in Table I. As seen from these results, both the whole samples differ little from one another in their MWDs. GPC data for the sample fractions of M- and HT-series, gained by fractionation with preparative GPC, are also summarized in Table I. For convenience in later discussion, the same code number, e.g., M-1 and HT-1, was affixed to each fraction of M- and HT-series, collected at the same retention time.

From Table I it is seen that the fractions of M- and HT-series having the same code number possess almost the same molecular weight and the ratios of weight-average to number-average molecular weight, M_w/M_n, calculated from GPC data for all the fractions, are lower than 1.1. The values of M_n and M_w/M_n calculated for R45M and R45HT on the basis of fractionation data by preparative GPC combined with analytical GPC data for each fraction are further listed in the lowest row of the table. These values are in

TABLE I
Fractionation Results of R45M and R45HT by Preparative GPC

R45M				R45HT			
Code	M_n	M_w/M_n	Wt frac. (%)	Code	M_n	M_w/M_n	Wt frac. (%)
M-1	27,300	1.07	1.2	HT-1	29,000	1.09	1.4
M-2	18,000	1.07	5.3	HT-2	19,600	1.08	5.7
M-3	12,400	1.08	8.1	HT-3	13,500	1.08	8.5
M-4	9,300	1.08	10.0	HT-4	9,800	1.08	9.8
M-5	7,100	1.09	11.7	HT-5	6,900	1.09	11.3
M-6	5,600	1.10	12.9	HT-6	5,400	1.09	11.8
M-7	4,300	1.09	13.8	HT-7	4,100	1.09	11.5
M-8	3,200	1.07	11.9	HT-8	3,200	1.07	11.5
M-9	2,500	1.06	9.0	HT-9	2,500	1.06	8.9
M-10	1,900	1.05	6.0	HT-10	1,900	1.05	7.1
M-11	1,400	1.04	3.9	HT-11	1,500	1.05	4.3
M-12	1,100	1.04	2.5	HT-12	1,200	1.04	2.9
M-13	900	1.04	1.6	HT-13	900	1.04	1.9
M-14	700	1.05	0.9	HT-14	700	1.06	1.4
M-15	600	1.04	0.5	HT-15	600	1.06	0.9
M-16	500	1.05	0.5	HT-16	500	1.07	0.6
M-17	400	1.04	0.3	HT-17	400	1.04	0.4
R45M	3,400	1.99	—	R45HT	3,100	2.23	—
Calcd[a]	3,290	1.88	—	Calcd[a]	3,070	2.10	—

[a] Values calculated on the basis of fractionation data by preparative GPC combined with analytical GPC data for each fraction.

good agreement with those directly obtained for the whole samples. This may be good evidence for high performance of the separation made by preparative GPC.

Characterization Results by TLC

Since it was impossible to chromatograph all of the sample fractions on one chromatoplate, comparative TLC experiments were conducted by dividing the samples into three groups; namely, a low, an intermediate, and a high molecular weight group, which correspond to code numbers 17–10 ($400 < M_n < 2000$), 10–5 ($2000 < M_n < 7000$), and 5–1 ($7000 < M_n < 30{,}000$), respectively.

Low-Molecular-Weight Group. First, six samples originating from each one of R45M and R45HT having the code numbers 17–15 were subjected to TLC in an ascending manner together with the whole sample R45M for comparison. The developer used was a ternary system $CCl_4/CHCl_3$/THF having a composition 75/75/9 by volume. The result is shown in Figure 2. Figure 3 shows chromatograms obtained for the fractions having the code number 15–10, R45M and R45HT with a ternary system CCl_4/Bz (benzene)/THF (75/75/13).

Before we discuss the assignment of final smears appearing on the chromatograms, the following two points are worth mentioning: One is a result of our previous work that nonfunctional polybutadienes migrated up to the solvent front, regardless of the type of microstructures,[16] when developers with polarities similar to those of this study were used, and the other is that the contents of nonfunctional polybutadiene in R45M and R45HT were

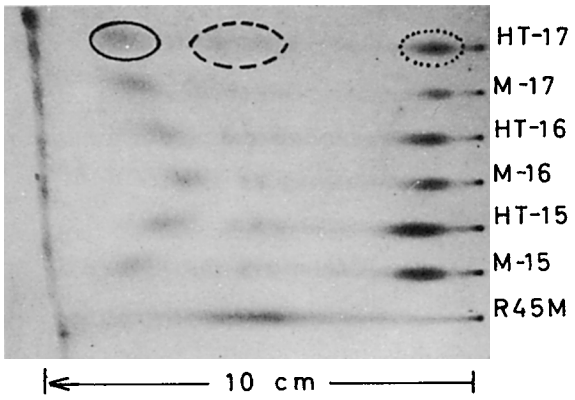

Fig. 2. TLC chromatograms of R45M and fractions having the code numbers 17–15. Enclosures of solid, broken, and dotted line indicate smears to be assigned to antioxidant, mono- and difunctional species, respectively.

estimated by a separate analysis to be negligibly small, say lower than 3%. The latter information was obtained by using "thin layer-FID-chromatography," which is described in our previous paper.[10] Here FID designates flame ionization detector.

The results mentioned above will allow us to argue the assignment of final smears without taking the nonfunctional component into consideration. Thus we will tentatively assume that every chromatogram observed above may be characterized by three final smears, except for another smear which remains immobile on the starting level and has been often seen in

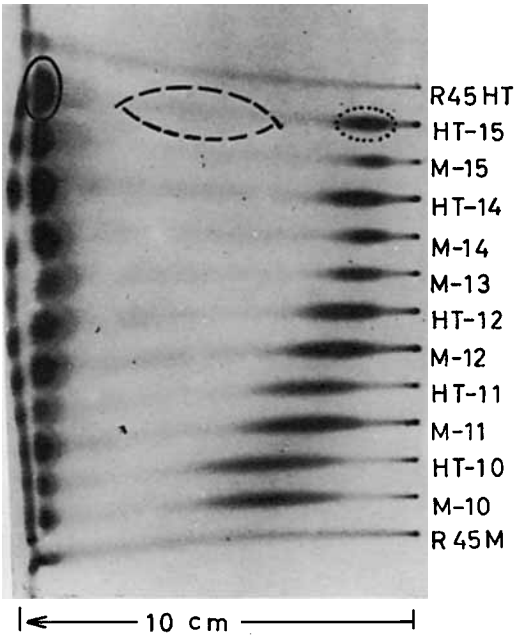

Fig. 3. TLC chromatograms of R45M, R45HT, and fractions having the code numbers 15–10. Enclosures have the same meanings given in the previous figure.

TLC for samples of diene polymers.[16] As to identification of this smear, discussion will be made at the end of this subsection.

The smear showing the highest R_f was easily assigned to antioxidant contained in the sample fractions by chromatographing a reference sample. For the other two smears, however, we had no possibility for direct assignment since no reference sample with known functionality was available. Under this circumstance, the following two observations became important for the assignment. One is that the smear showing the lowest R_f seems to be the major component, as anticipated from its density on the chromatogram, while the other is that the average functionalities of R45M and R45HT were 2.1 and 2.3, respectively. These allow us to reasonably assign the lowest smear to the difunctional species. Once such an assignment is done, then one may logically assign the intermediate smear to the monofunctional.

Further it is noticed in every chromatogram that the intermediate smear shows much longer broadening than does the lowest. This trend may be interpreted as follows: Adsorption of the monofunctional component onto the stationary phase should be weaker than that of the difunctional under the development conditions studied here[6] so that the molecular weight dependence of R_f for the former component will become more prominent than that for the latter. Through this interpretation one may find another endorsement for the assignments made above, even though it is indirect.

In this connection we should further note that the chromatograms for R45M and R45HT, seen in Figures 2 and 3, respectively, exhibit widely broadened smears emerging from the starting level without being separated into discrete smears as in the case of sample fractions. This may be attrib-

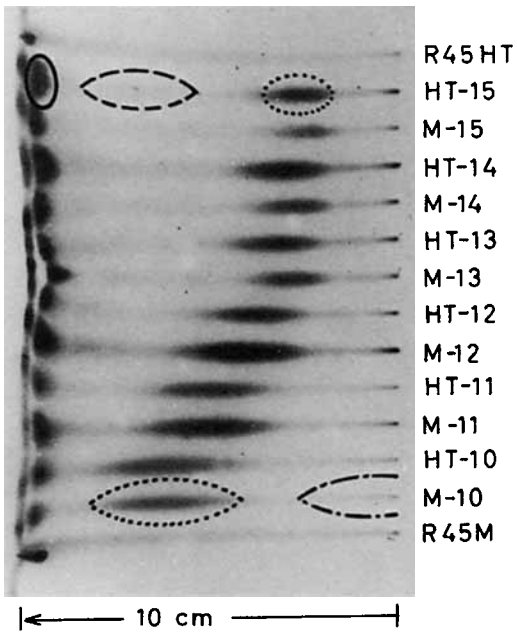

Fig. 4. TLC chromatograms of R45M, and R45HT, and fractions having the code numbers 15–10. Enclosure of one-dotted line indicates a smear to be assigned to polyfunctional species while the others have the same meanings given in a previous figure.

uted to broad molecular weight distributions of the commercial samples.

Now we will come back to the problem of smears remaining immobile on the starting level. Looking at the smears, we can find upward tailings, which are indicative of a possibility that there exist some polyfunctional species. To investigate the presence of such species, we have applied another development condition to the fractions with code numbers 15–10, viz., we employed a more polar ternary $CCl_4/CHCl_3$/THF (75/75/13) than that used to obtain Figure 3. The resultant chromatograms are shown in Figure 4. As seen from the figure, the upward tailing of immobile smears becomes more prominent being associated with further migration of the smears assigned to the difunctional species. This result may indicate that the sample fractions contain polyfunctional components but at very low contents. By the term "polyfunctional species" we mean components having higher functionalities than 3.

From the foregoing observations we may conclude that the low-molecular-weight group is composed of a larger amount of the difunctional, a small amount of the monofunctional species, and an extremely small but detectable amount of polyfunctional species. Furthermore, it should be mentioned that no remarkable difference in the functionality distribution between fractions of M- and HT-series having the same code number was observed.

Intermediate-Molecular-Weight Group. This group involved fractions having the code numbers 10–5 ($1900 < M_n < 7000$), which compose the central portion of MWDs of R45M and R45HT. Chromatograms obtained with a ternary system CCl_4/Bz/THF (100/100/10) for the fractions are shown in Figure 5. Assignments of final smears appearing in each chro-

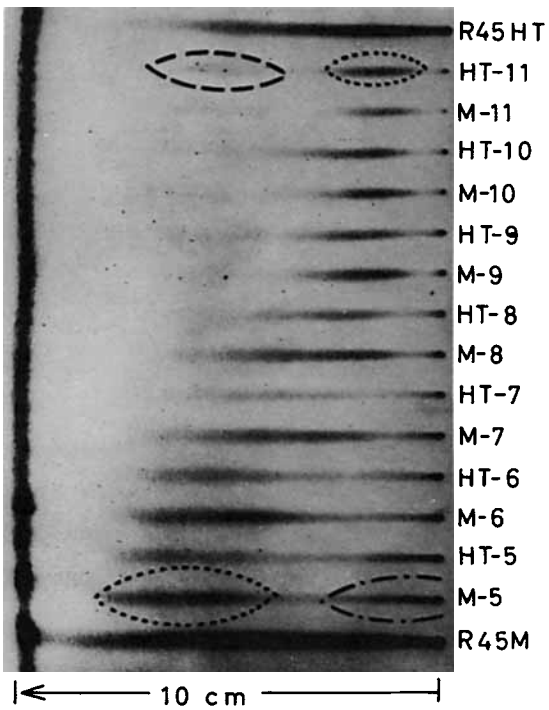

Fig. 5. TLC chromatograms of R45M, R45HT, and fractions having the code numbers 11–5. Smears due to antioxidant were washed out by a development with methanol.

TABLE II
Component Fractions of Di- and Polyfunctional Polybutadiene

Fraction	Difunctional (%)	Polyfunctional (%)	M_n
M-7	82	18	4,300
HT-7	76	24	4,100
M-6	74	26	5,600
HT-6	66	34	5,400
M-5	63	38	7,100
HT-5	50	50	6,900
M-4	22	78	9,300
HT-4	10	90	9,800
M-3	Trace	~100	12,400
HT-3	0	100	13,500

matogram were made according to the same consideration as described in the previous subsection. Again we find the difunctional species as the main component. Features of these chromatograms observed for fractions having the code numbers smaller than 7 are twofold: One is that the upward tailings from the starting level become more distinct with increased molecular weight (decrease in the code number) and the other is that the final smears to be assigned to monofunctional species tend to disappear when the molecular weight increases beyond those of M-8 and HT-8 (3200).

Now provided that the former chromatographic feature is indicative of an increase in the amount of polyfunctional species, a comparative analysis was carried out for the content of di- and polyfunctional species in each fraction. To this end, the chromatogram was subjected to the densitometric scanning in a manner previously described[11,15] so that the total density (photographic blackness) caused by each smear could be evaluated. The results are summarized in Table II. As recognized in the table, ratios of the polyfunctional to difunctional species steeply increase for both the M- and HT-series as the molecular weight increases. Such a tendency for the HT-

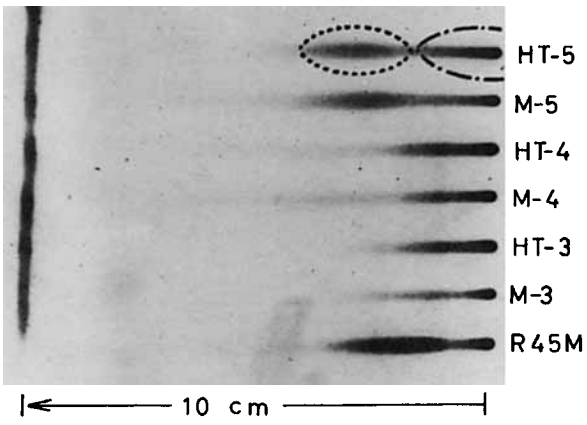

Fig. 6. TLC chromatograms of R45M and fractions having the code numbers 5–3 obtained after antioxidant had been washed out.

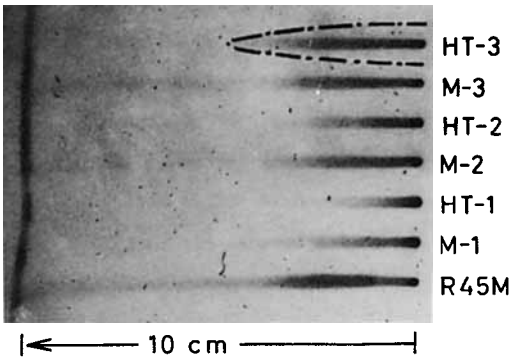

Fig. 7. TLC chromatograms of R45M and fractions having the code numbers 3–1 obtained after antioxidant had been washed out.

series is much stronger than for the M-series. These findings will be further justified below by investigating the high-molecular-weight group.

High-Molecular-Weight Group. In order to obtain further evidence to the decreasing tendency of difunctional species with the molecular weight, sample fractions coded 5, 4, and 3 were chromatographed with a ternary system CCl_4/Bz/THF (50/50/3), while those coded 3, 2, and 1 with the same ternary system but having a more polar composition (50/50/4). The chromatograms for the former and latter are shown in Figures 6 and 7, respectively. From Figure 6 we can see that the difunctional species tend rapidly to disappear with increased molecular weight. The relative densities of di- to polyfunctional species for M-3 and HT-3 were determined and are

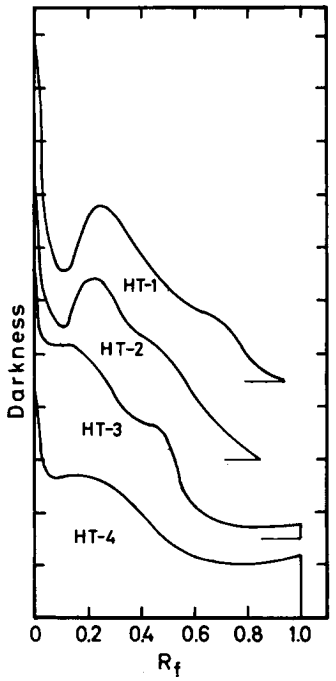

Fig. 8. Densitometric scanning traces for the fractions of HT-1, HT-2, HT-3, and HT-4.

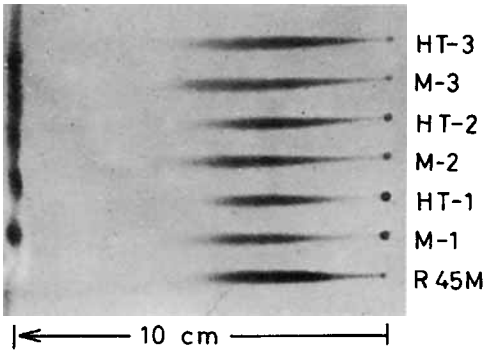

Fig. 9. TLC chromatograms obtained with a concentration gradient manner for R45M and fractions having the code numbers 3–1. (Antioxidant was washed out.)

also listed in Table II. On the other hand, the difunctional species was no longer detected for sample fractions of M- and HT-series coded 2 and 1 as shown in Figure 7.

Further separation of the polyfunctional species into components has been attempted by changing the composition of developer. Although we were unsuccessful in such separation as showing discrete smears, we experienced that the densitometric scanning of chromatograms thus obtained exhibited some peaks and shoulders in their traces, which might suggest the presence of plural components in the polyfunctional species. An example of these results is illustrated in Figure 8. This motivated us once again to try the separation by applying a concentration gradient procedure,[11] viz., the development was initiated with an equibinary system CCl_4/Bz (100 mL), to which THF (20 mL) was continuously added while the solvent front reached 10 cm above the starting level. In this way the sample fractions of M- and HT-series having the code numbers 3–1 were chromatographed. The result is given in Figure 9. Even though these chromatograms appeared not to indicate any special feature by themselves, the densitometric scanning revealed a distinct difference between the M- and HT-series as shown in Figures 10–12. Migration of each fraction of HT-series is more strongly

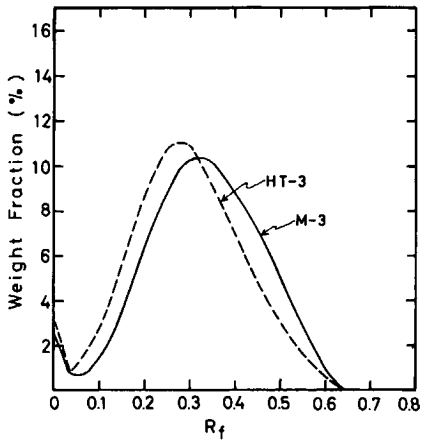

Fig. 10. Comparison of densitometric scanning traces between M-3 and HT-3.

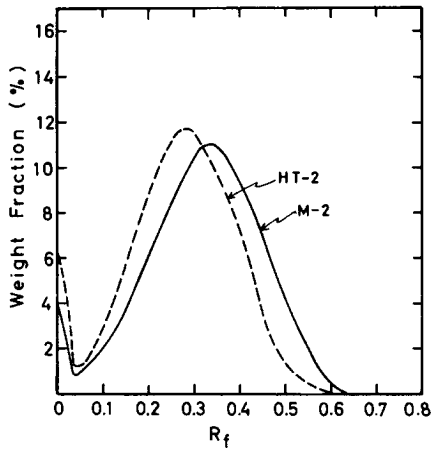

Fig. 11. Comparison of densitometric scanning traces between M-2 and HT-2,

retarded than that of the M-series, and this implies that the high-molecular-weight group of the HT-series is, on the average, richer in components having functionalities higher than 3 when compared with that of M-series.

CONCLUSION

Results obtained with GPC and polarity-controlled adsorption TLC for R45M and R45HT are summarized below.

1. No decisive difference in the MWD and the functionality distribution was found between these commercial products, except for their average functionalities, i.e., 2.1 and 2.3 for R45M and R45HT, respectively.

2. Low-molecular-weight fractions ($400 < M_n < 2000$) recovered from both the samples are composed mainly of the di- and monofunctional species. The former may be the main component.

3. For fractions belonging to the intermediate-molecular-weight group ($2000 < M_n < 7000$), which originate from the center part of MWDs, the difunctional species is distinctly regarded as the main component and the

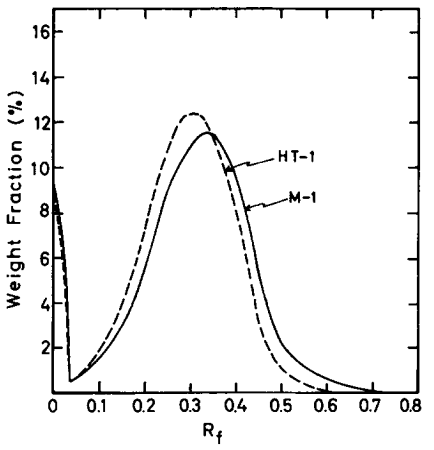

Fig. 12. Comparison of densitometric scanning traces between M-1 and HT-1.

monofunctional species tends to disappear as the molecular weight goes to higher while the polyfunctional species tends to increase. Ratios of the polyfunctional to difunctional species steeply increase with the molecular weight, and the tendency for the HT-series is much stronger than for the M-series.

4. High-molecular-weight fractions ($7000 < M_n < 30{,}000$) contain the polyfunctional species as the main component. Further separation of polyfunctional species into components was unsuccessful, but its content in the HT-series was found distinctly higher than in the M-series.

On the basis of these observations we may draw a conclusion that a decisive difference between R45M and R45HT consists specifically in the functionality distribution within the high molecular weight range beyond 7,000, i.e., the content of polyfunctional species in R45HT is clearly higher than in R45M. According to this conclusion, further study was conducted in order to understand the difference in mechanical and viscoelastic properties observed for solidified products of R45M and R45HT. This result will be seen in a subsequent paper.

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