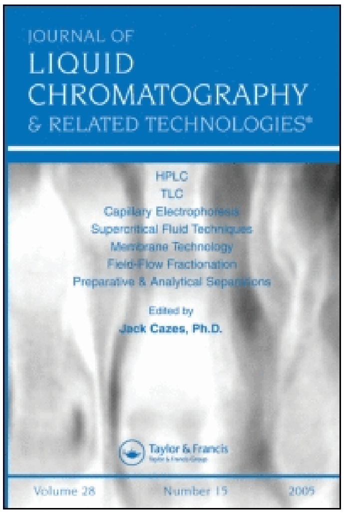

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R. Amato[a]; G. Marot[ab]
[a] Atochem Group Elf Aquitaine Cerdato, France [b] GRL-SNEA, ARTIX, France

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FUNCTIONAL CHARACTERIZATION OF HYDROXY-POLYBUTADIENES

R. AMATO AND G. MAROT*
Atochem
Group Elf Aquitaine
Cerdato, 27470 Serquigny, France

ABSTRACT

Analysis of hydroxyl functionalized polymers requires accurate knowledge of both molecular weight and functionality distributions. Usual average characterization such as viscosity (Brookfield and hydroxyl equivalent of the whole polymer, are not sufficient to represent product quality. Size exclusion chromatography, even with dual detection, is also limited in its capacity to characterize this type of macromolecules consequently their mechanical behaviour. Separation according to functionally has been achieved using stepwise elution from silica gel. The various problems encountered during analysis and the data finally obtained on HTPB using infrared spectroscopy are discussed.

INTRODUCTION

The major objective of this work has been the understanding of problems relating to the separation of

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(*) Present address : GRL-SNEA, BP 34, LACQ - 64170 ARTIX (France) functionalized prepolymers on a polar stationary phase. HTPB, now produced and sold by our company allows for a good illustration of an analytical application of adsorption column chromatography (1, 2). Several years ago, our research group succeeded in separating laboratory made products by size exclusion chromatography using UV and RI detectors after derivatization (3). But we concluded that the evolution of dn/dc and perhaps the absorption coefficient ϵ UV change along the molecular weight distribution (MWD). Thus the ratio between UV and RI response for a given hydrodynamic volume depends upon precise chemical structure and composition. We chiefly need informations at the boundaries i.e., in the low and high molecular weight regions. However, under these conditions, analysis becomes impossible since at the same time detector output is very low - due to low polymer concentrations in this field - and highly dependant upon response coefficients dn/dc and ϵ UV. Such analysis cannot be expected to yield accurate results but can, at best, indicate qualitative trends.

In the experiments described in this paper, it was decided to use an approach similar to that published by LAW (4). Polymer fractionation is carried out via stepwise low pressure elution from silica gel. The aim of the complete work is to propose a "high pressure method" to perform the same separation.

EXPERIMENTAL

Materials

- GPC solvent was THF supplied by MERCK (Darmstadt, RFA) stabilized with di-tert-butyl-paracresol and filtered through MILLIPORE (Milford, MA-USA) membranes type FH porosity 0.5 μm.

- GPC solutions were made using stabilized eluent and were filtered through GELMAN SCIENCES (Ann Arbor, MI-USA) membranes porosity 0.2 μm.

- Narrow distribution standards were purchased from Polymer Laboratories (Shrosphsire, UK) for polytetrahydrofuran.

- HTBP probes were laboratory made products supplied by ATOCHEM (Paris, France).

- Adsorption chromatography solvents were CCl4 supplied PROLABO (Paris, France), CHCl3 supplied by CARLO ERBA (Milan, Italy). Alcohol employed was a mixture of 95 % C2H5OH and 5 % isopropyl alcohol both supplied by CARLO ERBA.

- Adsorption chromatography stationary phase was silica gel Kieselgel 70 150 mesh purchased from MERCK (Darmstadt, RFA).

Adsorption chromatography

As described by LAW (4), a glass column (Ø30 - L 600 mm) was slurry packed with silica gel. 150 g of stationary phase was placed in suspension in a mixture composed of 63 % CHCl3, 4 % alcohols, 33 % CCl4. The polymer is dissolved in pure CCl4 (5 % w/v) and eluted by gravity under nitrogen ; in these conditions adsorption occurs (Fig. 1). Then the solvent schedule for one run, as shown in Table 1, leads to an increasing mobile phase polarity and a stepwise desorption for macromolecules. One gram of HTPB is separated in 40 samples with a recovery range ca 90 %. The complete process including evaporation and infrared characterization not considering SEC, lasts for approximately two days.

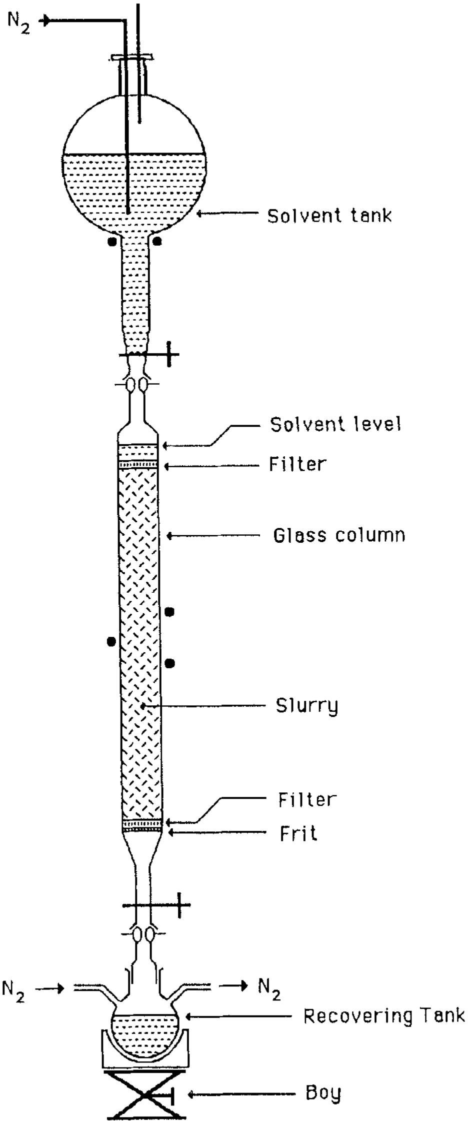

FIGURE 1. Chromatographic column scheme

Table 1 : Solvent schedule

Solvent		Volume (cm3)	Samples
CCl4		1000	S1 to S10
CCL4/CHCL3	(90/10)	100	S11
	(80/20)	100	S12
	(60/40)	300	S13 to S15
	(40/60)	100	S16
	(20/80)	300	S17 to S19
CHCL3		600	S20 to S25
CHCL3/C2H5OH	(99/1)	100	S26
	(98/2)	100	S27
	(96.5/3.5)	100	S28
	(95/5)	300	S29 to S31
	(90/10)	100	S32
	(80/20)	100	S33
	(70/30)	100	S34
	(60/40)	100	S35
	(50/50)	100	S36
	(25/75)	100	S37
C2H5OH		500	S38 to S42

Infrared measurements

Infrared data were obtained from a NICOLET 60 SX Fourier Transform infrared spectrometer. All measurements were carried out in CCl_4 solution using 2 cm path length cells. Characteristic IR absorption bands for Polybutadiene are presented in Table 2. Assuming a homogeneous distribution of 1.4 trans structures during the fractionation, calculation of polymer equivalent weights can be performed from a single calibration curve. Such curves have been obtained from two unfractionated samples taking into account absorbance at 967 cm^{-1}. Similar results in polymer equivalent weights are obtained at 3077 cm^{-1} ($-CH = CH_2$). These structures are present in the base polymer at a concentration of 20 %, however, this concentration can vary with molecular weight to reach 25 % for the higher end of MWD. Good agreement between data obtained from the two different calibration curves should also represent a separation according to functionality and not SEC.

Size exclusion chromatography

- Columns : Polymer Laboratories, mixed bed 60 cm, 500 Å and 100 Å, 30 cm.

- Solvent delivery : WATERS model 510.

- Injector : automatic sampler WATERS model WISP 710.

- Concentration detectors : Differential refractometer WATERS model R 410, uv spectrometer with fixed wavelength (254 nm) WATERS model 440.

Date acquisition and treatment were carried out using a computing system composed of a KEITHLEY 195 digital voltmeter, a

Table 2 : Bands in HTPB spectra

(from BINDER J.L, J.P.S part A vol 1, pp 47-58 (1963))

micro-meter	cm-1	Origin
3,25(a)	3077	CH stretch of CH2=CH
3,32(a)	3012	CH stretch of cis -CH=CH
3,45(a)	2900	CH stretch of CH2
3,4	2841	CH stretch of CH2
5,4(a)	1850	Overtone of CH2=CH
6,05(a)	1660	C=C stretch of cis -CH=CH2
6,8-6,9(a)	1640	C-C stretch of CH2=CH
6,10(a)	1470	CH2 def(b)
7,05(a)	1418	CH in plane def (c) of CH2=CH
7,10(a)	1408	CH in plane def (c) of cis -CH=CH
7,38	1355	CH of trans -CH=CH; also in 1,2A,S,I (b)
7,55	1325	in 1,2A,S,I (b)
7,63	1311	CH of cis -CH=CH
7,65	1307	in 1,2A,S,I (b)
7,75	1290	in 1,2A,S,I (b)
8,1	1235	in all spectra
8,3	1205	in 1,2,I (b)
8,8	1136	in 1,2,S (b)
9	1111	in 1,2,I (b)
9,25	1081	in emulsion and cis and trans CH=CH
9,3	1075	in 1,2 I,S (b)
9,5	*1053*	*high trans 1,4 (cristallinity)*
10	1000	high cis 1,4
10,05(a)	995	CH out of plane of CH2=CH
10,34(a)	967	CH out of plane of trans -CH=CH
10,98(a)	910	CH2 out of plane of CH2=CH
11,4	877	in 1,2 I (b)
11,7	855	in 1,2 S (b)
12,4	806	in 1,2 I (b)
12,5	800	in some high cis 1,4
12,9	775	*cristallinity band of high trans* 1,4
12,7	787	in 2,2 S (b)
13,5	740	cis CH=CH ,1,2 A, S (b)
14,1	709	1,2 I(b)
14,4	695	1,2 I (b)
14,8	675	1,2 A,I (b)
15	667	1,2 S (b)

a These assignment established by olefin spectra.

b Here 1,2,a,s,i,means atactic,syndiotactic,and isotactic polybutadiene syndiotactic and isotactic bands taken from Natta's spectra, may be in error by up to 0,04 micron

c Def. means deformation

KEITHLEY 705 multichannel scanner (Cleveland OH - USA) and a HEWLETT PACKARD HP 9816 computer (Palo-Alto, CA - USA). Data storage and processing were performed using GPC software developed at ESPCI a french national research laboratory (*).

RESULT AND DISCUSSION

Fractionation

Let us describe the elution profile shown in Figure 2. The elution volume represents an increasing polarity scale from CCl_4 to C_2H_5OH. When the eluent polarity increases, higher functionalized parts of the whole polymer must be eluted. Each 100 cm^3 step corresponds to a certain amount of fractionated HTPB, indicated in milligrams on the y - axis (IR-determination).

As regard the complete profile, different regions can be identified corresponding to the four major peaks and three areas between them. Under one peak or between two peaks, an assumption is made that the separated macromolecules have a roughly similar functionality. This leads to fractions composed of the various samples in each of these regions. For example, during run A, forty two samples of 100 cm^3 were obtained, that yielded seven fractions according to approximate functionality. After fractionation, each of the forty two samples were dried by solvent evaporation ; evaporation being the greatest time consuming part of this method.

(*) J. LESEC, 10 Rue Vauquelin, Paris 75005 (France)

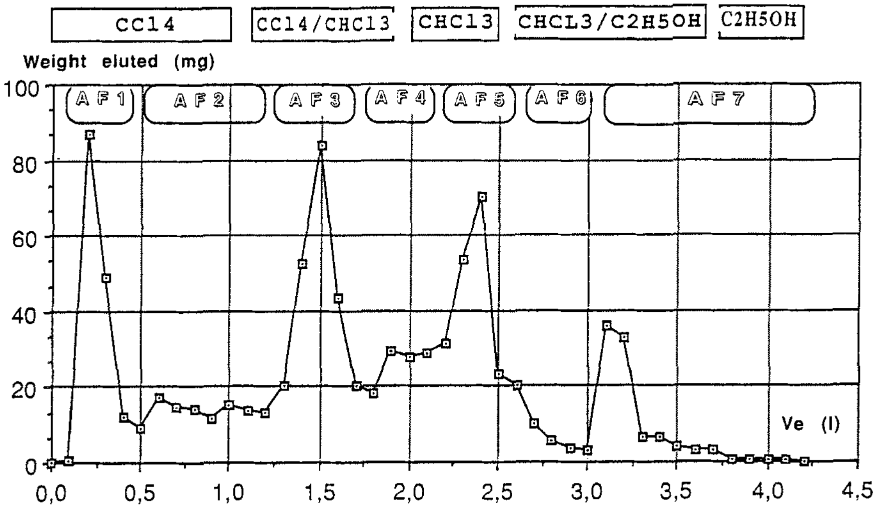

FIGURE 2. Elution profile

Experiments were also complicated by the high tendency, for this polymer to crosslink when in thindry films. Thus, after full evaporation, solubilization and infrared measurements were performed without delay.

The next step is to further separate one particular fraction or a combination of fractions using a chromatographic column with a higher activity. LAW (4) describes this change in active adsorption sites with the composition of primary slurry. Experiments were carried out under such conditions but a precise determination of activity is difficult. Published method concerning activity characterization of alumina (5) was performed in our case and led to good results. Figure 3 indicates reproducibility obtained during our trials over only one liter of eluent and tow different columns (Runs A and B).

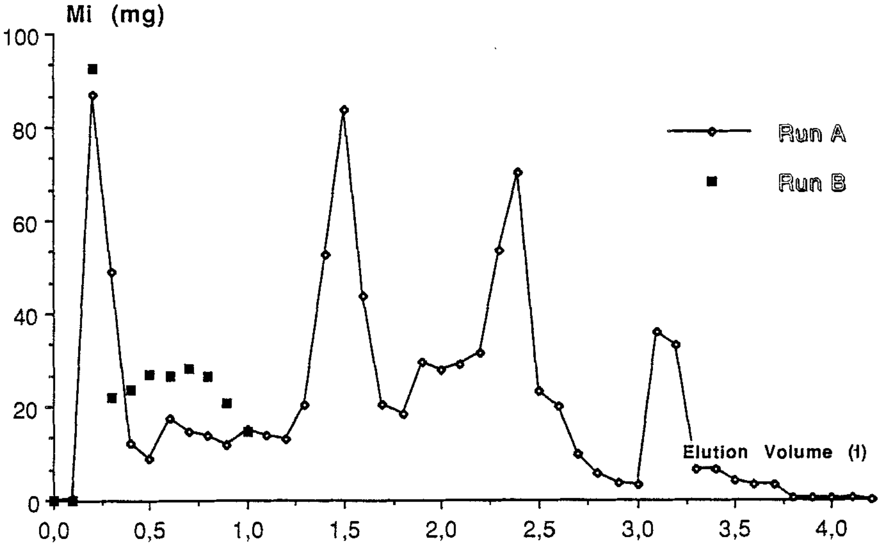

FIGURE 3. Reproducibility

Nota : Five runs have been achieved for this work. Each run leads to 40 samples - named S. Which are combined, in relation with the elution profile, in 6 or 7 fractions - named F.

The following code number is adopted :

- Si : S for Sample
  i is the sample number in chronological order during a run
- n Fm : F for Fraction
  n is the letter indicating the run A, B ...
  m is the number of the fraction, obtained by samples arrangement, in chronological order during run n
- ni Fm : i for further separation of fraction nFm

Infrared characterization

Polymer equivalent weights

Calibration curves plotted from data obtained with two HTBP and for different maximum peak absorption lead to satisfactory results. Table 3 shows good agreement between the data obtained by the three methods. It points out the potential of the infrared analysis for checking the first part of the separation. The recovery range lies from 80 to 90 % according to columns activity.

Hydroxyl equivalent weights

Hydroxyl equivalent weight was determined by chemical method for the two previous whole polymers. In the following these polymers are used as standards for infrared calibration curves. Their maximum OH peak absorption were found to be at 3620 cm^{-1}. For fractions 2 to 6 infrared spectra exhibit identical maxima and measurements were performed according to the previously method. But for fractions 1 and 7 OH absorption maxima occur respectively at 3635 and 3630 cm^{-1}. This information point out the presence of different microstructures (6, 7, 8, 9) which implies that infrared data based upon absorption coefficient are not good. Therefore we decide to combine fractions AF1 and AF2 to perform another separation with a higher activity column (Fraction AF7 was destroyed during IR analysis). Non functional material was found

Table 3 : Comparison of weights obtained by three different methods

	Polymer equivalent weights by (IR)		
	967 cm-1	3077 cm-1	weighing
Fraction	**Q2**	**Q1**	**Q3**
AF1	148,6	158,2	164,6
AF2	118,8	111,6	122,0
AF3	220,6	216,6	211,0
AF4	104,1	106,8	107,0
AF5	198,1	199,0	222,0
AF6	22,3	16,7	21,5
AF7	94,8	111,2	124,0

to be present in fractions AlFl and AlF3 (3 %) and maximum peak absorption for AlF2 was at 3620 cm^{-1}. This new analysis demonstrates the poor selectivity of the first system and implies that there certainly exists a mixture of non, mono and polyfunctional species in the fractions (1, 2).

All results are summarized in Table 4, and in spite of the foregoing observations agreement between whole polymer data and that calculated from fractionation is reasonable. The best results can be obtained when each sample is separated over at least two columns with increasing activity. But we may conclude that accurate analysis requires a very long time incompatible, for instance, with plant control laboratories.

Size exclusion chromatography of fractions (Runs A and Al)

Average molecular weights are summarized in Table 4. But these values do not represent a good characterization for such multidistributions samples (Fig. 4). The porosity of silica stationary phase is such that SEC can occur event during the adsorption process. For a given hydroxyl equivalent weight, a low weight average molecular weight (Mw) sample is eluted after the higher one (AlF3 after AlFl). For a given Mw, it is the hydroxyl equivalent weight that governs the elution process AF3 before AF5. GPC measurement demonstrate that separation seems mainly affected by functionality and that dn/dc must change from a fraction to another. If one considered row KRI in table 4, KRI represents approximately the refractive index increment necessary to perform GPC calculations. Accuracy for this value (about 7 %) implies that

Table 4 : General results (runs A,A1)

Fractions	**Weight eluted mi** (mg)	**% recovered** Initial weight of whole polymer (1g)	**Mwi** (g.mole-1)	**Mni** (g.mole-1)	**I(OH)i** (meq/kg)	**Fi=Mni*I(OH)i**	**KRIi**
AF1	148,6	14,9	9830	5560	-	-	3,1
AF2	118,8	11,9	4020	3120	-	-	3,3
A1F1	26,5	2,7	5060	3010	0	0,0	-
A1F2	192	19,2	6090	2590	510	1,3	-
A1F3	2,5	0,3	3040	840	0	0,0	-
AF3	220,6	22,1	3890	2650	820	2,2	3,7
AF4	104,1	10,4	6840	3070	930	2,9	3,6
AF5	198,1	19,8	4250	1570	1300	2,0	3,2
AF6	22,3	2,2	2770	910	2800	2,5	3,9
AF7	94,8	9,5	4350	1000	3700	3,7	-
TOTAL:	**861**	**86,1**					

	Run A	**whole polymer**
I(OH)= $\Sigma(mi*I(OH))/\Sigma mi$	1215,42	860
Fi= $\Sigma(mi*Fi)/\Sigma mi$	2,14	1,95

$$\mathbf{KRI} = \frac{\text{Chromatogram area}}{\text{Amount of polymer injected}}$$

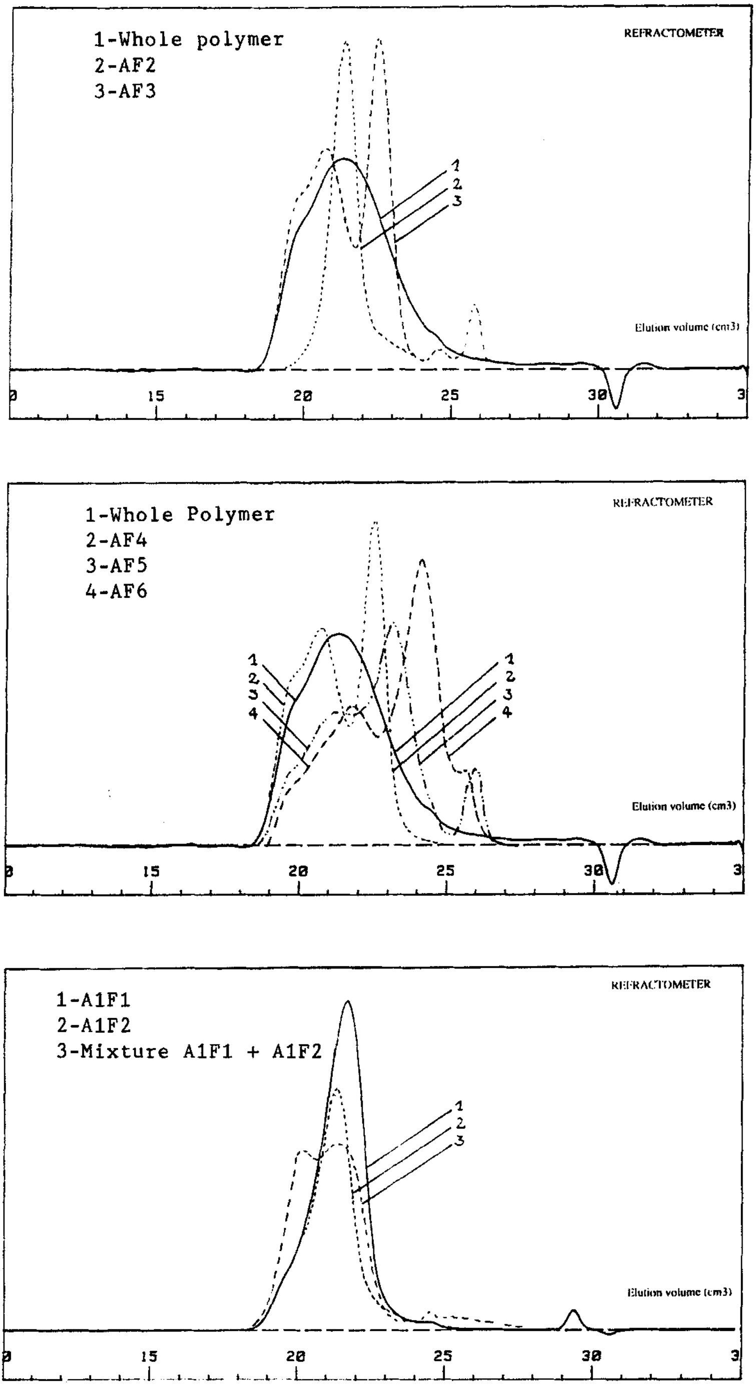

FIGURE 4. GPC of fractions (Runs A,A1)

hydroxyl content drastically disturbs light propagation in these short chains solutions. But variation across whole polymer molecular weight distribution remain lower because polydispersity for each fraction is very high. The exact influence of such effects on average molecular weight calculation has not been determined.

CONCLUSION

Knowledge of both functionality and molecular weight distributions is necessary if one wants to better understand the improvement of mechanical behaviour of any resin synthetized from the prepolymers. Analytical technique, published by LAW, brings out the main difficulties encountered during the two dimensional separation. Recent advance in polymer characterization by adsorption chromatography column or thin layer (10, 11) suggest that this method could be extrapolated to high performance, high pressure liquid chromatography ; now we are working in that way.

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