

## The Determination of Unsaturation in Ethylene Propylene Terpolymers and Butyl Rubber with Pyridinium Bromide Perbromide

MARJORIE E. TUNNICLIFFE, *Dunlop Research Centre, The Dunlop Co. Ltd., Birmingham 24, England*

### Synopsis

The reagent pyridinium bromide perbromide (PBPB) has been investigated for the determination of unsaturation in model olefins and in polymers of low total unsaturation. Model olefins give 92%-100% reaction for a 1-hr reaction period. Ethylene propylene terpolymers react quantitatively without substitution or elimination and without second addition reactions when the termonomer unit is 1,4 hexadiene, methylene norbornene, ethylidene norbornene, or cyclooctadiene. Dicyclopentadiene terpolymers react incompletely. These reactions take place in carbon tetrachloride/10% methanol solution, the reagent being added as a methanolic solution. Iodine chloride can also be used under specified conditions for the more reactive termonomer units in this solvent mixture. Under the same conditions the PBPB reagent reacts stoichiometrically with butyl rubber, without second addition or substitution reactions. The unsaturation results also agree with those obtained using bromine or iodine monochloride in carbon tetrachloride solution, but both of these reagents give slight substitution reactions.

### INTRODUCTION

Pyridinium bromide perbromide, first described and investigated by Rosenmund and Kuhnenn,<sup>2,3</sup> has been used in acetic acid solution as a brominating agent by Rosenmund et al.<sup>4</sup> Later Rowe et al.<sup>5</sup> used it in conjunction with a mercury catalyst to determine conjugated unsaturation. They obtained a constant value for the unsaturation of tall oil over a range of conditions, which suggests that the reagent does not produce a second addition reaction. Wilson and Nisbet<sup>6</sup> found that the reagent gave correct values for the unsaturation of model olefins and motor oils. Their reactions were conducted in an acetic acid/carbon tetrachloride solution.

PBPB is more freely soluble in methanol than in acetic acid and remains soluble on adding carbon tetrachloride to about a 12-fold excess. Ethylene propylene diolefin terpolymers (EPDM) remain in solution when up to 10% v/v of methanol is added. It is thus possible to hold polymer and reagent in a common solution of 90/10 v/v carbon tetrachloride/methanol. In this present study, methanolic PBPB directly replaces the iodine monochloride of the previous study.<sup>1</sup> The investigation includes the effect of time of reaction and of amount of excess reagent. Model olefins have also

been studied. Some checks have been obtained by including in the study terpolymers for which a satisfactory unsaturation result may be obtained with iodine monochloride.

There are other suitable solvent systems for this reaction. For instance, butyl rubber dissolved in a minimum of carbon tetrachloride and diluted with dichloromethane can be reacted with PBPB dissolved in methanol/1,2-dichloroethane 1/3 v/v without insolubilisation of the reagent or polymer at any stage, and with the same result for the unsaturation value. Methanol/*o*-dichlorobenzene 1/3 v/v is also a suitable solvent for the reagent.

With slight modification of the solvent system, the reaction with PBPB can be used to determine the unsaturation of diene polymers. This will be the subject of a further communication.

The corresponding tetraalkyl ammonium compounds were also considered. These are made by reaction of the tetraalkyl ammonium halide with elemental bromine in methanolic solution. The perbromide precipitates and solids can be made with varying bromine contents. On adding excess of bromine, a compound containing one molecule of bromine to one molecule of tetraalkyl ammonium halide precipitates, as determined by the titer of the compound with thiosulfate after addition of sodium iodide in alcoholic solution. The tetraethyl and tetrabutyl chlorides and bromides were also converted to their perbromides. All, however, proved to have a lower solubility in methanol/carbon tetrachloride mixture than the pyridinium compound, which was therefore the preferred reagent for this study.

## EXPERIMENTAL

### Materials Used

Pyridinium bromide perbromide solution is made by dissolving the solid in analytical-grade methanol. The solution is assayed by titration with sodium thiosulfate solution after addition of an aqueous solution of potassium iodide. A period of at least 1 hr is allowed before use to allow for possible reaction with impurities in the solvent. The solution slowly loses strength, and should be titrated with each batch of determinations. A 0.2*N* solution is suitable.

Iodine monochloride solution is made by dissolving the solid in analytical-grade carbon tetrachloride to make a 0.2*N* solution. It is tested in the same way as pyridinium bromide perbromide. The solution after the initial 1-hr period remains stable for two to three weeks. (If the iodine monochloride has an appreciable iodine content it may be purified by fractional crystallization, the iodine being concentrated in the liquid fraction.)

The olefins used as models for the terpolymers were of a pure grade, and they were assayed by gas chromatography. The polymers were either commercially available or made in these laboratories.

### Reaction of Pyridinium Bromide Perbromide with Olefins and Polymers

Samples of unvulcanized ethylene-propylene terpolymers are extracted with acetone to remove antioxidant, and dried. Accurately weighed 0.5-g portions are dissolved in 45–50 ml of carbon tetrachloride by shaking at room temperature. For the time curves, larger weights, 2.0–2.5 g, are taken and dissolved in the corresponding volume of carbon tetrachloride, to be made up to 200 or 250 ml after adding the reagent. The olefins are dissolved in carbon tetrachloride so that their concentration in the reaction solution is about 0.002*M*. The methanolic solution of PBPB is made up to a concentration which gives an approximately onefold excess of reagent in 5 ml. A 5-ml portion is pipetted into the olefin or polymer solution, the latter being swirled to avoid precipitation. If any localized precipitation occurs, the precipitate is redissolved by stoppering and shaking immediately afterward. For the time curves the volume of reagent added is 10% of the volume of the polymer or olefin solution, and aliquots are withdrawn at set times. After leaving the reaction mixture in the dark for the set time, the excess PBPB is reacted with aqueous potassium iodide and the liberated iodine titrated with 0.05*M* thiosulfate. A blank with solvent only is run alongside, the difference between the blank and sample titers giving the total iodometric titer. All titrations are expressed in terms of normality or milliequivalents rather than molarity since it appears with this brominating reagent there is not an exact stoichiometric relationship between the pyridinium bromide perbromide and the active bromine.

## RESULTS AND DISCUSSION

### Reaction of Pyridinium Bromide Perbromide with Model Olefins

Several olefins reacted with PBPB for 1 hr, and reacted with iodine monochloride under the same conditions. The results are given in Table I. They show the PBPB reagent to be slightly less reactive than iodine mono-

TABLE I  
Reaction of Model Olefins with PBPB and ICI

Olefin	% Reaction	
	with PBPB	with ICI
1-Decene (CH <sub>2</sub> =CH—)	97.5	100
1-Decene (CH <sub>2</sub> =CH—), more reagent	99.5	100
2,4,4-Tri-Me-pentene-1 (CH <sub>2</sub> =C(CH <sub>3</sub> ) <sub>2</sub> —)	99	104
1-Me-cyclohexene (C=C(CH <sub>3</sub> ))	92	106
4-Me-pentene-2 trans (—HC=CH—trans)	96	97
Cyclooctene-1 (CH=CH)	94	100

chloride and to give a reaction not greater than 100%. The PBPB would thus appear not to be giving further addition reactions. In some cases the 1-hr reaction period may not be sufficient at the reagent concentration used.

### Ethylene-Propylene Terpolymers

It was shown in a previous paper<sup>1</sup> that the level of unsaturation in ethylene-propylene terpolymers incorporating an unsaturated termonomer can be determined for some termonomer units by reaction with iodine monochloride. When a more reactive termonomer unit is incorporated this procedure yields high results, due to a splitting out reaction of the dihalide followed by a further addition reaction at the newly formed double bond.<sup>1</sup> The following results on different types of EPDM were obtained using PBPB reagent.

**Nordel EP Terpolymer.** The Nordel terpolymer contains a *trans*-CH=CH group, as judged by its infrared spectrum, and behaves in the same way as a 1,4-hexadiene terpolymer made in these laboratories. Reaction with PBPB of this terpolymer gives an unsaturation figure slightly less than that obtained with ICl under the same conditions. As this terpolymer gives a slightly high result with ICl,<sup>1</sup> the PBPB is giving a substantially correct figure. When the reaction is allowed to proceed for varying lengths of time, it is seen (Table II) to be complete in 1/2 hr and to remain unchanged for 4 hr. These results show that the PBPB reagent is giving a true measure of the unsaturation, since slower second-addition reactions are not taking place. The results also show that no substitution is taking place in the EP chain since this too would result in a slow increase in the amount of reagent consumed.

TABLE II  
Reaction of Nordel 1040 Terpolymer with PBPB for Various Times

Time, hr	Unsaturation, wt-% 1,4-hexadiene
1/4	3.4
1/2	3.70
1	3.70
1 1/2	3.74
4	3.73

**EP-Methylene Norbornene Terpolymer.** The reaction of this terpolymer with PBPB, when followed in respect to time, is found to be complete in 1/2 hr, so again no substitution reaction takes place (Table III). An aliquot of polymer solution reacted with ICl for 1 hr gives the same result, although a splitting-out reaction occurs. Thus, for a methylene norbornene terpolymer, pyridinium bromide perbromide gives a stoichiometric reaction.

TABLE III  
Reaction of EP-Methylene Norbornene Terpolymer with PBPB for Various Times

Time, hr	PBPB used, mEq
1/4	0.580
1/2	0.586
1	0.588
2	0.585
4	0.583

**EP-Ethylidene Norbornene Polymers.** Aliquots of a stock solution of an EP-ethylidene norbornene terpolymer reacted with varying amounts of PBPB including insufficient amounts for complete reaction, and after a 1-hr reaction throughout, give the results in Table IV. They indicate an increase of only 3% in PBPB consumption with a two-fold excess of reagent. An experimental terpolymer containing 50% by weight ethylidene norbornene gives a slight increase with time in the amount of PBPB consumed, amounting to about 1.2% per hour of the unsaturation figure (Table IV). Thus, at the 5-7 wt-% ethylidene norbornene level, the further reactions of the termonomer unit should be negligible. Iodine chloride with this polymer gives an increase with time in the amount of reagent used amounting to 5% per hour of the unsaturation figure with a 200% excess of reagent (reduced somewhat by iodine formation).

**EP-Cyclooctadiene Terpolymer.** It is not possible to determine the unsaturation in ethylene-propylene-cyclooctadiene terpolymers directly with either iodine monochloride or bromine, the figure increasing continuously with time.<sup>1</sup> Using the PBPB reagent, the unsaturation figure remains constant with time, the reaction being complete in a 1/2-hr period (see Table V). PBPB is thus reacting stoichiometrically with the cyclooctadiene terpolymer.

TABLE IV  
Reaction of EP-Ethylidene Norbornene Terpolymers with PBPB

Polymer	Time, hr	PBPB added, MEq/g	PBPB used, mEq/g
Low EN	1	0.122	0.122
	1	0.243	0.243
	1	0.972	0.580
	1	1.684	0.594
	1	2.215	0.603
	1	3.106	0.611
	1	3.106	0.611
50 wt-% EN	1/2	13.7	7.25
	1	14.7	7.7
	2	14.7	7.95
	4	14.7	8.15
	1/4	34	7.5
	1	34	8.0
	4	34	8.3

TABLE V  
Reaction of an EP-Cyclooctadiene Terpolymer with PBPB

Reaction time, hr	Unsaturation, wt-% cyclooctadiene
1/2	3.30
1	3.35
2 1/2	3.35

**EP-Dicyclopentadiene Terpolymer.** An EP-dicyclopentadiene terpolymer reacts stoichiometrically with ICl, so that an alternative reagent such as PBPB is not needed. Three aliquots of a solution of a DCP terpolymer, reacting respectively with ICl for 1 hr, PBPB for 1 hr, and PBPB overnight, in the same way as for the previous terpolymers, gave respectively 100%, 50%, and 80% reaction. Thus, PBPB is not a suitable reagent for use with DCP terpolymers.

### Solvent Effect

The reaction between an unsaturated unit and iodine monochloride has been shown to be much faster in carbon tetrachloride solution than in carbon tetrachloride/acetic acid solution.<sup>7</sup> It is thus highly likely that the addition of methanol to carbon tetrachloride will, in itself, slow down the reaction, so that in the case of a reactive termonomer units the second-addition reaction responsible for high results may be reduced to negligible proportions. Comparisons of PBPB and ICl in carbon tetrachloride/methanol solution over a range of concentration of reagent to  $-C=C-$  ratio give the results shown in Table VI for a cyclooctadiene terpolymer. Bromine and iodine monobromide are also included. The figures show a reduced reaction for the terpolymers with ICl, whereas bromine maintains a higher figure and iodine monobromide reacts incompletely in the 1-hr period. The unsaturation figure for all three halogens varies, however, with the amount of excess reagent added, whereas PBPB gives a more constant figure. The addition of methanol is therefore not sufficient of itself to cut out the second-addition reactions. However, over a restricted range

TABLE VI  
Comparison of Reagents in Carbon Tetrachloride/Methanol  
Solution for EP-Cyclooctadiene Terpolymer

Reaction conditions <sup>a</sup>	Wt reacted, g	Added, mEq/g	Used, mEq/g
PBPB; CCl <sub>4</sub> /10% MeOH v/v	0.50	0.910	0.285
ICl; CCl <sub>4</sub>	0.50	1.085	0.435
ICl; CCl <sub>4</sub> /10% MeOH v/v	0.50	1.085	0.275
ICl; CCl <sub>4</sub> /10% MeOH v/v	0.50	1.40	0.29
Br <sub>2</sub> ; CCl <sub>4</sub>	0.50	1.21	0.30
Br <sub>2</sub> ; CCl <sub>4</sub> /10% MeOH v/v	0.50	1.21	0.32
IBr; CCl <sub>4</sub> /10% MeOH v/v	0.50	1.08	0.20

<sup>a</sup> All reactions in 50 ml CCl<sub>4</sub> plus additions.

of conditions ICl could be used in carbon tetrachloride/10% methanol solution to give a result within 5% of the correct value. A routine procedure could be worked out on these lines.

### Butyl Rubber

Various procedures have been used for the analysis of butyl rubber. These include ozonolysis followed by molecular weight determinations of the original rubber and the fragments,<sup>8</sup> analysis of butyl containing C<sup>14</sup>-tagged isoprene by the same procedure, and then by an iodine/mercuric acetate method,<sup>9</sup> iodine/mercuric acetate reaction to give comparative figures,<sup>10,11</sup> and reaction with iodine chloride under strictly controlled conditions.<sup>12</sup> Reaction with iodine bromide, ozonolysis followed by determination of the carboxylic acid formed, and the iodine/mercuric acetate procedure have been compared,<sup>13</sup> as have the iodine/mercuric acetate method and ozonolysis with protection of the main chain, followed by determination of the total ketone formed.<sup>14</sup> Methoxy mercuriation has been used with success,<sup>15</sup> with an accuracy of  $\pm .23\%$ .

It is clear from reading these papers that absolute results are hard to obtain. For example, an ozonolysis method gave a much lower value than an iodine monochloride procedure and the iodine/mercuric acetate procedures require the use of arbitrary factors to convert iodine used to unsaturation values.

The foregoing results in this paper indicate the possibility of pyridinium bromide perbromide giving absolute results for unsaturation in butyl. A sample of Butyl 301 was therefore taken for the investigation. It was found possible to dissolve this in carbon tetrachloride at a 2% concentration, and a stock solution was made up at this concentration after acetone extraction. Aliquots of this solution were taken for separate determinations, which were conducted in the same way as for the ethylene-propylene terpolymers. Results are given in Table VII.

The results in Table VII show that the addition reaction is complete in the  $\frac{1}{2}$ -hr period and that after this time there is no further reaction. Thus substitution and second-addition reactions are ruled out. In confirmation, the reaction was repeated with a 2.5-fold excess of reagent, and a figure of 1.92 wt-% was obtained, an increase of only 0.05 wt-%.

A comparison was made with the iodine chloride reaction. Lee's<sup>12</sup> published curves of the ICl used versus reagent excess show the conditions

TABLE VII  
Reaction of Butyl with PBPB for Various Times

Time, hr	PBPB used, mEq/g	Isoprene, wt-%
$\frac{1}{2}$	0.548	1.87
1	0.552	1.875
2	0.550	1.87
4	0.554	1.88

TABLE VIII  
Comparison of Solvent Systems for Butyl 301

Methanol/CCl <sub>4</sub> , wt-% isoprene	Methanol/Dichloroethane/CCl <sub>4</sub> , wt-% Isoprene %
1.88	1.89
1.87	1.90
1.92	1.95
1.92	1.94

under which a correct result is obtained with this reagent. When these conditions were used, the isoprene content obtained was 1.91 wt-%; with the same excess reagent as was used for the PBPB determinations, a result of 2.44 wt-% was obtained.

The results for PBPB show 1.88 wt-% is a maximum result, since any second-addition reaction would have to be subtracted from it. Comparison with the ICl results points to the absence of second-addition reaction with PBPB and confirm an appreciable second addition with a moderate excess of ICl.

TABLE IX  
Direct Comparison of PBPB and Bromine

Reagent	Time, hr	Amount added, mEq	Amount used, mEq	Isoprene, wt-%
PBPB	1	0.930	0.552	1.88
Br <sub>2</sub>	1	1.200	0.553	1.88
PBPB	1	1.014	0.309	1.88
Br <sub>2</sub>	1	1.200	0.309	1.88
PBPB	6	0.935	0.413	1.87
Br <sub>2</sub>	6	1.88	0.440	2.00

An alternative solvent system was compared directly with the carbon tetrachloride/methanol system used. It consisted of 25 ml of carbon tetrachloride, to dissolve the polymer, with 25 ml of dichloroethane, added later, then 5 ml of reagent dissolved in methanol/dichloroethane 1/2 v/v. This system was less liable to give precipitation of the polymer on adding the reagent solution. Results in Table VIII show good agreement between the two solvent systems.

A comparison was made between PBPB and elemental bromine, the latter in carbon tetrachloride solution. Pairs of determinations were run for 1 hr at two dilutions and for 6 hr. Results are shown in Table IX. They can be interpreted as showing that bromine also gives the correct figure for a 1-hr reaction time but that some further slow reaction also takes place. Confirmation was obtained by allowing the reaction to proceed for various periods of time. The bromine solution was added to a large volume of a 1.5% solution of butyl and 50 ml aliquots were withdrawn at set intervals.



The results are shown in Table X. The figures show a rise of about 2% per hour and give the same figure at zero time as the PBPB reagent, and thus confirm the results in Table IX.

Finally, the reaction with iodine monobromide was investigated. Aliquots of a 1.5% solution were reacted for 1½ and 6 hr with a solution of

TABLE X  
Reaction of Butyl with Bromine for Various Times

Time, hr	Br <sub>2</sub> added, mEq/g	Br used, mEq/g	Isoprene, wt-%
1/3	1.270	0.557	1.89
2/3	1.270	0.561	1.905
1	1.270	0.569	1.93
3½	1.270	0.588	1.995
5½	1.270	0.597	2.10

TABLE XI  
Reaction of Butyl with Iodine Bromide

Time, hr	IBr added, mEq/g	IBr used, mEq/g	Isoprene, wt-%
1½	1.44	0.585	1.99
6	1.44	0.629	2.14

TABLE XII  
Unsaturation Levels of Butyl Rubbers and Polyisobutene

Sample	PBPB added, mEq/g	PBPB used, mEq/g	Isoprene, molar %	Manu- facturers' figures, molar % isoprene
Polysar Butyl 100	0.235	0.059	0.74	0.65
Polysar Butyl 200	0.234	0.103	1.38	1.34
Polysar Butyl 301	0.175	0.108	1.51	1.52
Polysar Butyl 301	0.175	0.106	1.49	1.52
Polysar Butyl 450	0.254	0.159	2.23	
Enjay Butyl 268	0.264	0.121	1.82	1.5-2.0
Polyisobutene	0.162	0.003	0.04	

iodine bromide in carbon tetrachloride. Results in Table XI show an increase of titer at the rate of 1.7% per hour.

The extrapolated figure for zero time is 1.94 wt-% as compared with 1.88 wt-% for the PBPB reaction. Thus, iodine monobromide is reacting stoichiometrically, with a very small further slow reaction.

Several other butyl samples were examined and gave concordant results using PBPB reagent (see Table XII).

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