Hydroxyl-Terminated Polybutadiene. I. A Study of the Polymerization of Butadiene in the Presence of Hydrogen Peroxide

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ABSTRACT: The polymerization of butadiene in a solution of 1-butanol as a solvent and in the presence of hydrogen peroxide as an initiator was studied. The influence of four factors—polymerization temperature, concentration of the initiator, polymerization time, and stirring rate—on the yield, molecular weight characteristics, and the number-average functionality of the hydroxyl-terminated polybutadienes (HTPBs) were determined. Regression models which adequately fit the experimental data were obtained. On this basis, the optimum values of the most significant factors—polymerization temperature and concentration of the initiator for obtaining maximum yield of HTPB—were evaluated. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 2491–2496, 1997

INTRODUCTION

The preparation of terminally hydroxylated polybutadienes can be accomplished by anionic or free-radical polymerization.[1] The free-radical polymerization of butadiene in a solution and in the presence of hydrogen peroxide as an initiator appears to be a more economical route to these liquid rubbers. The reaction medium is a common organic solvent for the monomer and the initiator, and alcohols are particularly suitable to this purpose. Polymerizations are usually conducted for 2–4 h at temperatures within 90–130°C, yielding essentially water-white odorless liquid products.[2–7] The polymerization is initiated predominantly by HO• radicals. The key to achieving an effective difunctionality is the termination taking place predominantly by a combination of growing macroradicals. All chain-transfer reactions involving the solvent, initiator, polymer, and monomer occur as side processes. A significant side reaction is also the decomposition of hydrogen peroxide to HOO• and H•; however, the indicated reaction pathway is favored by a high temperature.[8] Consequently, the products are found to contain low molecular weight monofunctional polymers as well as high polymers containing two or more hydroxyl groups. In addition to the hydroxyl endgroups, small amounts of other oxygen-containing species, including aldehydes, ketones, carboxylic acids, hydroperoxides, and epoxides, have been detected.[4,5,9]

The commercial development of this technology[7] requires a specification of the conditions for the synthesis of terminally hydroxylated polybutadienes with definite functionality and molecular weight characteristics. However, the technical literature contains little basic information on polymerizations of this type. The conditions for preparation of hydroxyl-terminated polymers based on dienes of average molecular weight in the order of a few thousands and an average content of 2.1–2.3 hydroxyl groups per chain have mainly been reported.[1,3,6,8–13] Polymers containing hydroxyl groups up to 5 or even more have been found only

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Table I   Levels of Factors and the Responses of the Statistical Design of Experiments for HTPB Synthesis

	Factors								
Exp Runs	z_1 (mass %)	z_2 (°C)	z_3 (h)	z_4 (min^{-1})	y_1	y_2	y_3	y_4	y_5
1	5.00	120	4	1000	60.6	5250	6070	3.07	5.62
2	2.75	120	4	1000	54.3	5450	12,100	2.22	3.62
3	5.00	100	4	1000	36.5	5380	10,250	1.91	2.62
4	2.75	100	4	1000	17.5	4090	7900	1.93	2.74
5	5.00	120	2	1000	58.6	4660	9180	2.05	4.72
6	2.75	120	2	1000	50.6	6000	15,040	2.50	4.59
7	5.00	100	2	1000	30.3	4020	8420	2.09	3.00
8	2.75	100	2	1000	24.7	5390	8700	1.61	3.71
9	5.00	120	4	600	59.4	4830	11,930	2.47	3.32
10	2.75	120	4	600	59.0	5560	12,320	2.22	5.21
11	5.00	100	4	600	46.5	4180	8430	2.02	2.43
12	2.75	100	4	600	37.6	5920	10,470	1.77	2.96
13	5.00	120	2	600	60.6	4100	8240	2.01	4.00
14	2.75	120	2	600	38.6	5700	10,360	2.03	5.23
15	5.00	100	2	600	27.1	4890	8260	1.69	3.27
16	2.75	100	2	600	19.4	5110	8460	1.65	3.40

in some isolated cases.[14] The purpose of this article was to evaluate the significant factors and their optimal values for obtaining hydroxyl-terminated polybutadiene (HTPB) in the polymerization of butadiene in the presence of hydrogen peroxide.

EXPERIMENTAL

HTPB was prepared by free-radical polymerization of butadiene initiated by commercial H_2O_2 (32–35%) in 1-butanol as a solvent. Both the solvent and monomer were obtained from Neftochim Co. (Bulgaria), whereas H_2O_2 was a product of Fluka (Germany). For the polymerization, 85–102 cm^3 (94.8–113.8 g) H_2O_2 (32.2%) was dissolved in 1210 cm^3 (980 g) 1-butanol in a 5 L metal autoclave in a nitrogen atmosphere. Then, 2260 cm^3 (1410 g) butadiene was condensed under pressure. The stirring speed of the reaction mixture was adjusted within 600–1000 min^{-1}. The polymerization temperature was 95–120°C. After 2–4 h, the autoclave was cooled down and the reaction product was drained from the bottom. The product was stored overnight followed by decantation of the solvent. Liquid antioxidant Wing Stay K (Goodyear Co.) was added to the oligomer and the latter was concentrated in a liquid falling film.[15] HTPB was, consequently, purified before

use by evaporation under a vacuum at 40°C overnight. The experiments were carried out by using a factorial design of the first order and the second order, respectively.

The number-average ($\bar{M}_n$) and weight-average ($\bar{M}_w$) molecular weights of polymer samples were determined by GPC. The measurements were performed in THF solvent at 35°C in a 1 mL/min flow, using a Waters 200 gel permeation chromatograph equipped with four Ultrastyragel columns (1×10^6, 2×10^4, 1×10^4, and 1×10^3 Å pore size). The calibration curve was obtained with polystyrene standards having an $\bar{M}_w/\bar{M}_n$ < 1.1 in the molecular weight range of 470,000 to 1800. The hydroxyl groups' content was determined by acetylation.[10,16] The polymers were acetylated by excess acetic anhydride in dry pyridine (3 h, 100°C). The excess anhydride was hydrolyzed with water (1 h, 100°C) and the acetic acid received was titrated with alcoholic KOH using phenolphtalein as the indicator. The number-average functionality ($\bar{f}_n$) was calculated from the $\bar{M}_n$ value and the hydroxyl content (x_{OH}, mass %) using the following formula: $\bar{f}_n = \bar{M}_n \cdot x_{OH}/M_{OH} \cdot 100$, where M_{OH} is the molecular weight of the hydroxyl group.

RESULTS AND DISCUSSION

The effects of the initiator concentration (z_1), temperature (z_2), polymerization time (z_3), and stir-

Table II Regression Models, Standard Deviations, and *F*-criterion

Response Function	Mathematical Models	Standard Deviation	F_{cal}	F_{crit} ($\alpha = 0.05$)
y_1 (D, %)	$y_1 = 42.581 + 4.869x_1 + 12.631x_2 + 3.843x_3$	6.2	1.87	8.74
y_2 ($\bar{M}_n$)	$y_2 = 5021.88 - 383.13x_1 + 149.38x_2 - 128.13x_1x_2 + 208.13x_1x_3 + 135.62x_2x_4$ $+ 155.62x_1x_4 + 291.88x_1x_2x_4 - 230.62x_1x_2x_3x_4$	201.8	2.55	8.89
y_3 ($\bar{M}_w$)	$y_3 = 10{,}380 - 288.7x_1 + 1518.7x_2 + 803.7x_3 + 571.2x_4 - 267.5x_1x_2 + 775.0x_1x_3$ $+ 305x_1x_4 + 402.5x_2x_3 + 615x_2x_4 + 676.2x_1x_2x_3 - 283.7x_1x_2x_4 + 788.7x_1x_3x_4$ $+ 230x_1x_2x_3x_4$	502.8	4.96	9.55
y_4 ($\bar{M}_w/\bar{M}_n$)	$y_4 = 2.0775 + 0.2438x_2 + 0.1238x + 0.0950x_4 + 0.1163x_1x_2x_3 + 0.1038x_1x_2x_3x_4$	0.1786	2.66	8.79
y_5 ($\bar{f}_n$)	$y_5 = 3.7775 + 0.7613x_2 + 0.3175x_1x_4 + 0.3388x_1x_2x_4$	0.4635	3.55	8.74

ring speed (z_4) on the yield of the oligomer (y_1), the number-average molecular weight $\bar{M}_n(y_2)$, weight-average molecular weight $\bar{M}_w(y_3)$, index of polydispersity $\bar{M}_w/\bar{M}_n(y_4)$, and number-average functionality $\bar{f}_n(y_5)$ were studied.

The experiments were based on a 2^4 factorial design with z_1, z_2, z_3, and z_4, each at two levels. The values of these factors and the responses obtained in various experimental runs are listed in Table I.

These data were fitted to the response function:

$$y_i = f(x_1, x_2, x_3, x_4) = b_0 + b_1x_1$$
$$+ b_2x_2 + b_3x_3 + b_4x_4 + b_{12}x_1x_2$$
$$+ b_{13}x_1x_3 + b_{14}x_1x_4 + b_{23}x_2x_3 + b_{24}x_2x_4$$
$$+ b_{34}x_3x_4 + b_{123}x_1x_2x_3 + b_{124}x_1x_2x_4$$
$$+ b_{234}x_2x_3x_4 + b_{1234}x_1x_2x_3x_4 \quad (1)$$

where variables stand for the following ratios:

$$x_1 = (z_1 - 3.9)/1.1 \quad x_3 = (z_3 - 3)/1$$
$$x_2 = (z_2 - 110)/10 \quad x_4 = (z_4 - 800)/200 \quad (2)$$

The constants b_0, b_1, ..., b_{1234} were evaluated by the least-squares method. The mathematical models obtained which include statistically significant coefficients only are presented in Table II.

The analysis of the model equations (Table II) shows that the temperature is the most significant factor for the yield of the oligomer and its functionality. The next important variables are the concentration of the initiator and the polymerization time. The stirring rate appears to be a less significant factor. On the other hand, the interactions between the factors do not affect the yield of HTPB.

A relatively more complicated equation is obtained for the number-average molecular weight y_2. The negative sign of the coefficient at x_1 (concentration of initiator) shows an inversely proportional dependence between x_1 and y_2. The temperature is the significant factor and the stir number is the insignificant one in this case, too. However, the interactions between the factors have a strong effect on the number-average molecular weight. Perhaps, this is the reason for the impossibility of obtaining a low molecular weight polymer, solely by increasing the concentration of the initiator. The temperature also has influence on the weight-average molecular weight (y_3) and the polydispersity (y_4), respectively. It may be con-

Table III   Levels of Initiator Concentrations and Temperature

Factors	Upper Level +1	Base Level 0	Lower Level −1	Unit
Initiator concentration z_1 (x_1 in coded form) (mass %)	7	6	5	1
Temperature z_2 (x_2 in coded form) (°C)	115	105	95	10

cluded that one of the most significant factors influencing all characteristics of the polymerization product is the temperature.

The optimum levels of the significant variables, i.e., z_1 and z_2, were determined from experiments based on a 3^n statistical design. The values of factors z_3 and z_4 were $z_3 = 4$ h and $z_4 = 1000$ min^{-1}, which were accepted from the preliminary experiments.

The 3^n factorial design was chosen because the information obtained from it concerns both linear and quadratic components of the effects of the factors. The quadratic component may imply a maximum or minimum response at the same intermediate factor combination or at a point outside the range examined for some or all the factors, indicating a need for further work at the different set of levels.[17] Moreover, this design is quasi D-optimum and it allows one to obtain more precise estimations of the regression coefficients.

The actual values of the variables corresponding to the coded values are listed in Table III. Table IV shows the responses y_i of statistical design experiments. The results for the (y_i) at different values of z_1 and z_2 were fitted to the response function:

$$y_i = f(x_1, x_2) = A_1 x_1 + A_2 x_2$$
$$+ A_{12} x_1 x_2 + A_{11} x_1^2 + A_{22} x_2^2, i = 1, 2, 3, \ldots, 5 \quad (3)$$

where x_1 and x_2 are the coded forms for

$$x_1 = (z_1 - 6)/1 \quad x_2 = -(z_2 - 105)/5 \quad (4)$$

The constants A_0, A_1, A_2, etc., were estimated by using the least-squares method. By substituting them in eq. (3), we get the regression models presented in Table V. The standard deviations as well as the calculated and critical values of the F-criterion are also shown there. In all cases, F_{calc} is lower than F_{crit} and it can be concluded that the mathematical models adequately describe the process under study.

The dependence of the initiator concentration on the number-average molecular weight is presented in Figure 1. As can be seen, the number-average molecular weight (y_2) drops rapidly when both the concentration of initiator (z_1) and the temperature (z_2) increase in the studied experimental range. This behavior is in correspondence with the theoretical foundation of radical polymerization kinetics. The maximum amount of initiator which is necessary for obtaining a minimum molecular weight appears to be 7 mass %.

Calculations for the different y_i ($i = 1, 2, \cdots 5$) values can be performed by assigning arbitrary values for x_2 in the equations given in Table V and then by solving the resulting quadratic equations for x_1. This is shown in Figures 2–4.

It is interesting to note that the molecular weight distribution ($\bar{M}_w/\bar{M}_n$) becomes wider when the temperature and concentration increase (Fig. 2). This may be the result of the stronger influence of these two factors on $\bar{M}_n$ than on $\bar{M}_w$.

Table IV   The Responses of Factorial Design 3^2

Exp Runs	z_1 (mass %)	z_2 (°C)	y_1 (%)	y_2	y_3	y_4	y_5
1	7.00	115	36.8	2500	7780	3.11	3.89
2	6.00	115	67.9	2950	8650	2.93	2.95
3	5.00	115	75.3	3740	8660	2.32	2.07
4	7.00	105	61.3	3330	10,130	3.04	2.10
5	6.00	105	47.0	3400	9350	2.75	3.92
6	5.00	105	69.5	4150	8860	2.13	4.44
7	7.00	95	37.3	3730	9400	2.52	3.24
8	6.00	95	40.9	4220	10,100	2.39	3.92
9	5.00	95	29.2	4760	10,900	2.29	4.54

Table V   Regression Models, Standard Deviations, and *F*-criterion

Response Functions	Mathematical Models	Standard Deviations	F_{cal}	F_{crit} $\alpha = 0.05$
y_1 $(D, \%)$	$y_1 = 59.5 - 6.4x_1 - 0.37x_1^2 + 12.1x_2 - 11.6x_1x_2 - 11.4x_2^2$	124.8	6.07	9.28
y_2 $(\bar{M}_n)$	$y_2 = 3447 - 515x_1 + 215x_1^2 - 586.7x_2 - 52.5x_1x_2 + 60x_2^2$	31,769	1.99	9.28
y_3 $(\bar{M}_w)$	$y_3 = 9499 - 185x_1 - 78x_1^2 - 885x_2 + 155x_1x_2 - 198x_2^2$	714,630	0.09	9.55
y_4 $(\bar{M}_w/\bar{M}_n)$	$y_4 = 2.72 + 0.32x_1 - 0.12x_1^2 + 0.19x_2 + 0.14x_1x_2 - 0.05x_2^2$	0.02428	2.02	9.55
y_5 $(\bar{f}_n)$	$y_5 = 3.6 - 0.3x_1 - 0.2x_1^2 - 0.46x_2 + 0.78x_1x_2 - 0.04x_2^2$	0.80664	0.92	9.55

Figure 3 shows that the yield of HTPB slightly depends on the initiator concentration at low temperature levels. Any increase of temperature over 105°C results in an insignificant decrease of the
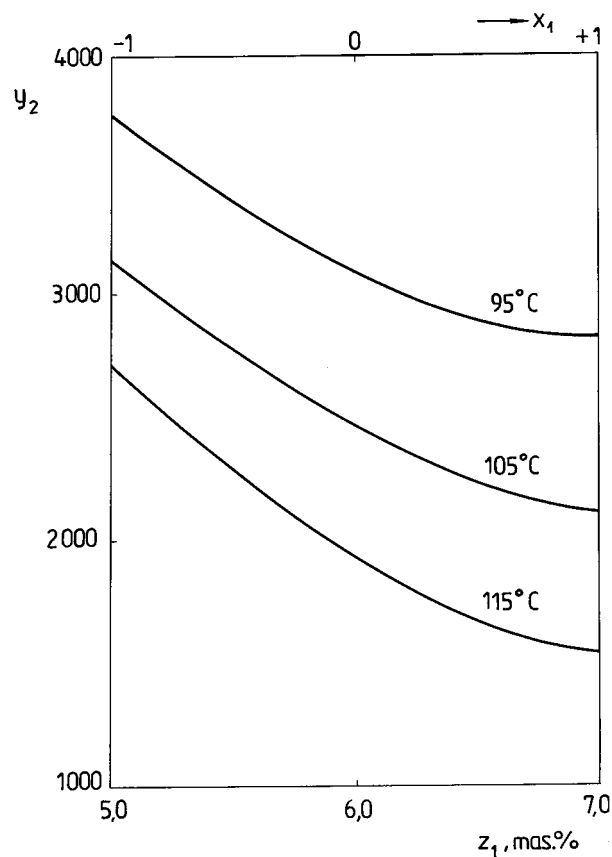

Figure 1   Number-average molecular weight $\bar{M}_n(y_2)$ as a function of the concentration of the initiator (z_1) at different values of temperature.

yield with increase of the initiator concentration. These results can be explained by the formation of low molecular products diluted in 1-butanol, whose amount was not taken into consideration. At the same concentration of the initiator, the yield of the oligomer increases and the number-average molecular weight decreases with increasing polymerization temperature (Figs. 1, 3, and 4).

Figure 4 also shows that the combination of the lowest number-average functionality and molecular weight values can be reached at the highest values of x_1. Under these conditions, the number-average functionality is about 3. It should be noted that a value of the number-average functionality close to 2 can be obtained when the temperature and initiator concentration are 105°C and 7%, or 115°C and 5%, respectively. Under these conditions, the values of $\bar{M}_n$ are 3330 and 3740, and at $\bar{M}_w/\bar{M}_n$, 3.04 and 2.32, respectively.
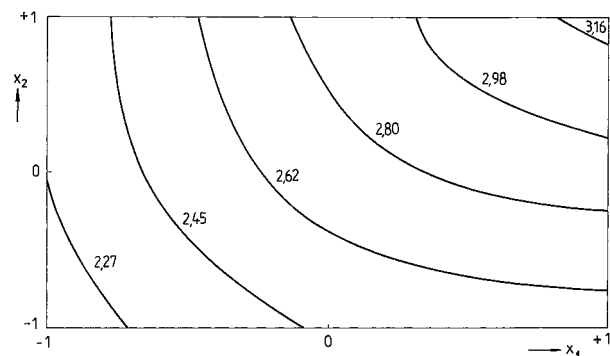
The optimum values of z_1 (concentration of the

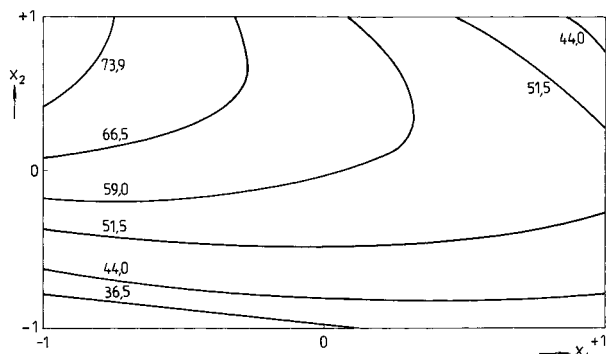**Figure 2**   Constant level curves for $y_4(\bar{M}_w/\bar{M}_n)$.

Figure 3 Constant level curves for y_1.

Figure 4 Constant level curves for y_2 (interrupted line) and y_5 (continued line).

initiator) and z_2 (temperature of polymerization) were determined by finding the maximum of the response function y_1 subject to the inequality constraints:

$$\text{Optimize} \quad y_1 = f_1(z_1, z_2) \rightarrow \text{maximum}$$

$$\text{Subject to} \quad 3000 < y_2 < 10{,}000$$

$$1 < y_4 < 3$$

$$2 < y_5 < 3$$

The maximum of this objective function was found by using the simplex method of Nelder and Mead.[18] As a result, the following ultimate optimum values of variables were obtained:

$$z_1 = -0.89(5.1\% \ H_2O_2) \quad y_1 = 75.9$$

$$z_2 = 0.95(114.5°C) \quad y_2 = 3620$$

$$y_4 = 2.65$$

$$y_5 = 2.63$$

These results were additionally experimentally confirmed.

CONCLUSIONS

The polymerization of butadiene with hydrogen peroxide for obtaining hydroxyl-terminated polybutadiene was studied. Based on the experiments and the modeling of the process, the significant factors and their optimum values for obtaining the maximum yield of the HTPB were determined. Regression models were obtained to de-
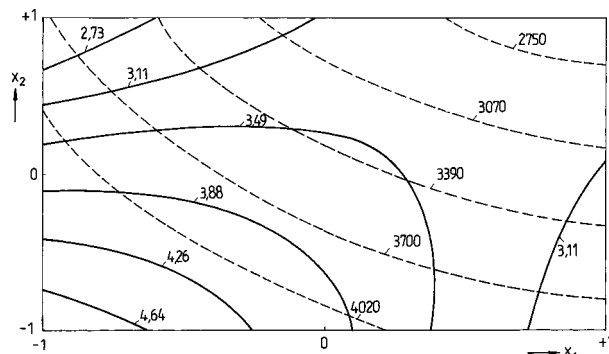
scribe appropriately the polymerization process. These models correlate reasonably well with the experimental data and they were used for estimating the significant factors and their optimum values.

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