Photochemical Chlorocarboxylation of Polyisobutylene

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A B S T R A C T

There have been reports about the studies of simultaneous chlorination and carboxylation of polyethylene affected by gaseous chlorine and maleic anhydride (MA) in carbon tetrachloride solution within the range of 90-110°C. In this study, photchemical chlorination of polyisobutylene (PIB) in the presence of MA, and, in particular, the kinetics of this process were investigated. Photochemical chlorocarboxylation of polyisobutylene was carried out in the mixture of carbon tetrachloride and chloroform. The order of the reaction with regard to reactant concentrations and the value of the reaction rate constant were found. By the method of quantitative description of substitution sites on the polymer chain, the ratio of the rate constants of the chlorination and carboxylation reactions was calculated. The effect of the neighbouring unit, i.e., a decrease in the chlorination rate under the accepting effect of maleic anhydride (scavenging effect) was observed. The time of the reaction corresponding to the maximum value of the scavenging effect was established.

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INTRODUCTION

There have been reports [1-4] about the studies of simultaneous chlorination and carboxylation of polyethylene affected by gaseous chlorine and maleic anhydride (MA) in carbon tetrachloride solution within the range of 90-110°C. The kinetics and mechanisms of photochemical reactions in various polymers in the absence of oxygen were studied at low temperatures [5]. Photocrosslinking of polyethylene in the presence of 9,10-anthraquinone was also studied [6]. In a more recent study,

thermo- and photo-oxidation of polyisobutylene was investigated [7].

The present work is concerned with the investigation of photochemical chlorination of polyisobutylene (PIB) in the presence of MA, and, in particular, of the kinetics of this process.

EXPERIMENTAL

Polyisobutylene (PIB) P-200 (molar mass 210,000 according to the characteristic viscosity) was purified by reprecipitation from n-hexane into isopropanol and then dried in vacuum at 50°C. Chlorine was dried by passing through the concentrated sulphuric acid. Its oxygen content is not higher than 0.05 percent. Maleic anhydride (MA) was purified by recrystallization from chloroform. To carry out chlorocarboxylation, the calculated amounts of chorine solution in CCl_4 and of MA solution in chloroform are added to the solution of the polymer in CCl_4. As a result, 2% solution of the polymer in the mixture composed of 80% vol. CCl_4 and 20% vol. $CHCl_3$ is obtained. Reaction was carried out in a cylinder shaped 500-mL jacketed two-necked vessel stirred by a magnetic stirrer under reflux. The reaction mixture is irradiated by an incandescent lamp (intensity of illumination-160 lux). The experimental procedure is as follows: As expressed above, the chlorine gas was first dried by passing through concentrated sulphuric acid, then dissolved in CCl_4. The undissolved excess of chlorine was removed by being absorbed by NaOH in an absorption vessel. The amount of chlorine dissolved was determined by iodometric method. This chlorine solution and the solution of MA in $CHCl_3$ were added to the solution of polymer in CCl_4. The reaction mixture thus prepared was placed in the reactor and the reaction was carried out at 20°C under inert gas atmosphere with illustration by a 200 Watt (160 lux) lamp until a clear solution was obtained. After this completion of the reaction, HCl was driven away by inert gas and the obtained polymer was precipitated by ethanol and then the polymer was dried by vacuum at 50°C. The obtained chlorocarboxylated PIB (CCPIB) contains various amounts of chlorine and carboxylic groups.

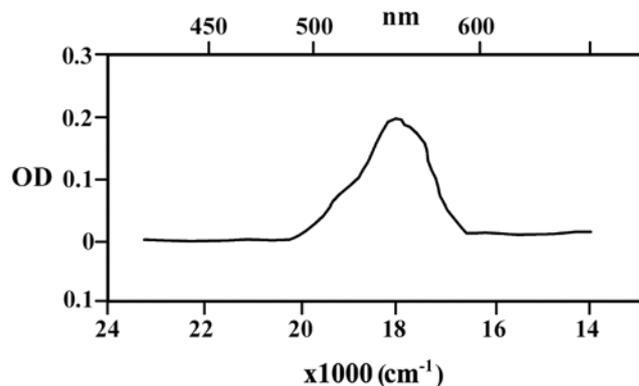The chlorine content was determined by Schniger method [8].

Figure 1. The intensity of colouring at 570 nm (Specord-UV-Vis).
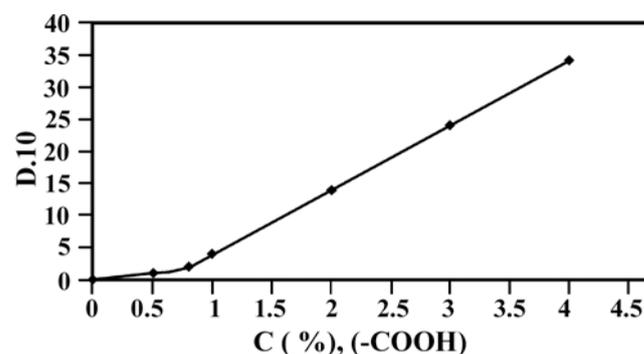

Figure 2. The calibration curve for determination of carboxylic groups.

The products of PIB chlorocarboxylation were analyzed by two methods in order to estimate the content of carboxylic groups:

(a) Titration of CCPIB benzene solution by standard alkali solutions in alcohol.

(b) UV-spectroscopy upon interaction of the polymeric solution with a dye.

CCPIB was titrated by a weak alkali, then it was neutralized with a weak acid in order to find all the reacted units of MA in an acidic form. The purified CCPIB (in the acidic form) was used for the interaction with a dyestuff, as was described in [9]. In the present work, Rhodamine-B was used as a dyestuff. Upon the interaction of the diluted benzene solution of CCPIB with the dyestuff, the solution acquires a pink colour. The intensity of colouration was measured by the spectrometer Specord-UV-Vis at 570 nm (Figure 1). The analogous procedure was carried out with acetic acid solution to build calibration curves (Figure 2). These curves were employed for ascertaining carboxylic

groups content in the samples.

RESULTS AND DISCUSSION

The IR-spectrum of CCPIB is illustrated in the Figure 3. The bands at 1720 and 1750 cm^{-1} belong to C=O bonds in the carboxylic groups. The large band at 2750-3500 cm^{-1} is related to OH- fragment of the carboxylic groups. The enlargement of these bands is apparently caused by hydrogen bonds of various lengths. The bands at 528, 696, 704 and 1228 cm^{-1} are due to CHCl-groups.

The kinetics of PIB chlorination in the presence of MA has been studied at $20^{o}C$. The intensity of illumination was 160 lux. The concentration of the polymer in the mixture of CCl_4 (80 % vol.) and $CHCl_3$ (20 % vol.) was equal to $(17.8-78.2) \times 10^{-2}$ mol/L, chlorine $(32.2-64.8) \times 10^{-2}$ mol/L and MA $(1-5) \times 10^{-2}$ mol/L.

To find the rate constant, it is necessary to determine the orders of the rate with regard to all of the reactants. From the series of experiments (Figures 4-6), it has been concluded that the reaction rate order with respect to the concentration of chlorine is about 1, with respect to PIB is 0.5, and with regard to MA would be zero. Therefore, the rate equation of PIB chlorination in the presence of MA may be written in the following form:

$$r = k\,[PIB]^{1/2}[Cl_2] \qquad (1)$$

hence,

$$k = r/([PIB]^{1/2}[Cl_2]) \qquad (2)$$

The calculated values of the rate constant as well as of the initial rate at various ratios of the reactants are given in Table 1.
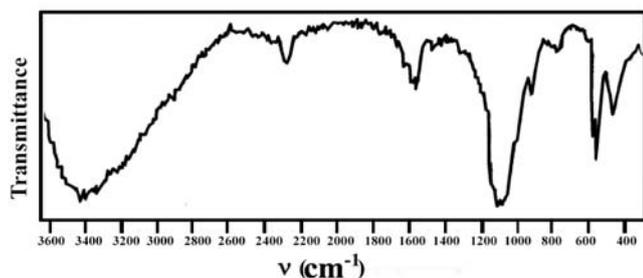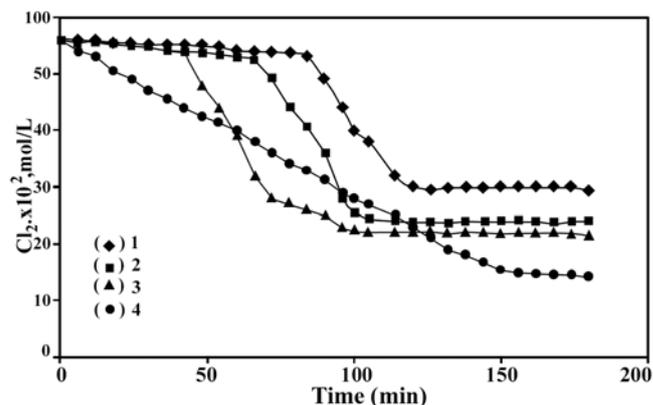

Figure 3. IR Spectrum of CCPIB.

Figure 4. Kinetics of PIB chlorination in the presence of MA in the mixture of 80 % (vol) CCl_4 and 20 % (vol) $CHCl_3$. The temperature is $20^{o}C$; the intensity of illumination is 160 lux. ((1)-$[PIB]_0 = 35.7 \times 10^{-2}$ mol/L; $[MA]_0 = 5 \times 10^{-2}$ mol/L (the mass ratio PIB:MA = 100:25), (2)-$[PIB]_0 = 35.7 \times 10^{-2}$ mol/L; $[MA]_0 = 3 \times 10^{-2}$ mol/L (the mass ratio PIB:MA=10:15), (3)-$[PIB]_0 = 35.7 \times 10^{-2}$ mol/L; $[MA]_0 = 10^{-2}$ mol/L (the mass ratio PIB:MA= 100:5), (4) $[PIB]_0 = 35.7 \times 10^{-2}$ mol/L; Ma is absent).

The kinetics of the process may be considered by the method of quantitative description of the sites in PIB chain which are occupied by chlorine and MA at a given time.

The sum of the sites in the PIB chain, where chlorination or carboxylation can take place, may be denoted as NO (the total number of sites). Under the accepted conditions of the reaction, the formation of the frag-
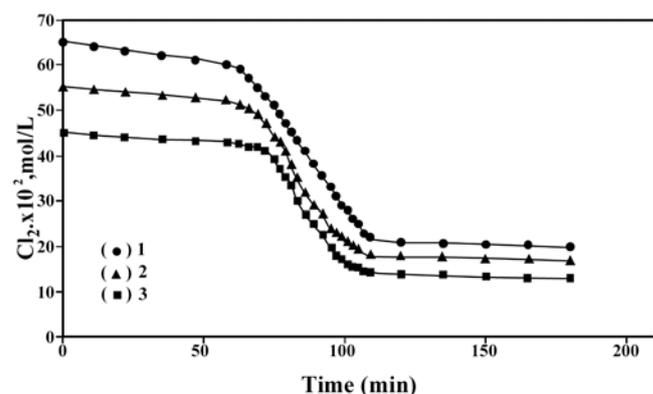

Figure 5. Kinetics of PIB chlorination in the presence of MA in the mixture of 80 % (vol) CCl_4 and 20% (vol) $CHCl_3$. The temperature is $20^{o}C$; the intensity of illumination is 160 lux. ((1)-$[PIB]_0 = 38.9 \times 10^{-2}$ mol/L; $[MA]_0 = 2.1 \times 10^{-2}$ mol/L), (2)-$[PIB]_0 = 35.7 \times 10^2$ mol/L; $[MA]_0 = 2.4 \times 10^2$ mol/L, (3) $PIB]_0 = 37.3 \times 10^2$ mol/L; $[MA]_0 = 2.2 \times 10^2$ mol/L,.
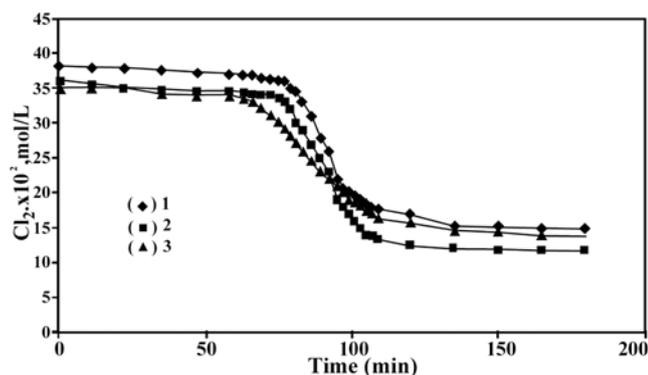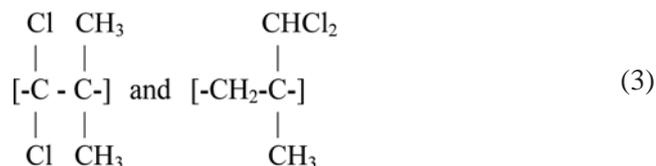
Figure 6. Kinetics of PIB chlorination in the presence of MA in the mixture of 80% (vol) CCl_4 and 20% (vol) $CHCl_3$. The temperature is 20°C; the intensity of illumination is 160 lux. ((1)-$[PIB]_0$= 17.8 × 10^{-2} mol/L; $[MA]_0$ = 1.8 × 10^{-2} mol/L, (2)-$[PIB]_0$ = 78.2 × 10^{-2} mol/L; $[MA]_0$ = 1.8 × 10^2 mol/L, (3)-$[PIB]_0$= 35.7 × 10^{-2} mol/L; $[MA]_0$= 1.8 × 10^{-2} mol/L).

ments is impossible, so only one site for replacement at each carbon atom is possible in the PIB chain. Therefore, the following relationship may be written:

$$
\begin{array}{cc}
\text{Cl} \quad \text{CH}_3 & \text{CHCl}_2 \\
| \quad | & | \\
[-\text{C} - \text{C}-] \quad \text{and} \quad [-\text{CH}_2-\text{C}-] \\
| \quad | & | \\
\text{Cl} \quad \text{CH}_3 & \text{CH}_3
\end{array}
\tag{3}
$$

$$N_0 = N_{Cl} + N_{MA} + N_V \tag{4}$$

Where N_{Cl} is the number of sites occupied by chlorine; N_{MA} is the number of sites occupied by the MA frag-

ment, and N_V is the number of vacant sites. The last equation may be transformed to such a form:

$$1 = \theta_{Cl} + \theta_{MA} + \theta_v \tag{5}$$

where

$$\theta_{CL} = \frac{N_{Cl}}{N_0}; \quad \theta_{MA} = \frac{N_{MA}}{N_0}; \quad \theta_V = \frac{N_V}{N_0} \tag{6}$$

In order to determine the ratio of PIB chlorination and carboxylation rate constants, the equation proposed in [3],

$$\theta_{CL} = k_{Cl}/k_{MA} [Cl_2]\ln\theta_{MAo}/(\theta_{MAo}-\theta_{MAt}) \tag{7}$$

was used for calculations.

The results of the corresponding calculations have been shown in Table 2.

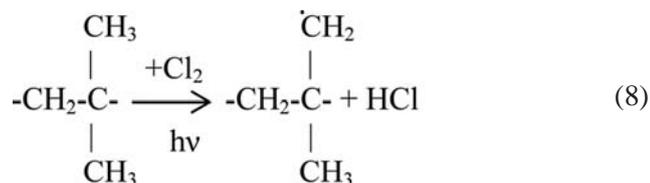The typical curves of θ_{Cl} and θ_{MA} change in the process of PIB chlorocarboxylation are shown in Figures 7 and 8. θ_{Clt} versus $\theta_{MAo}/(\theta_{MAo}-\theta_{MAt})$ dependency plot has been illustrated in Figure 9. This plot is approximated to straight line, the slope of which corresponds to the quantity $(k_{Cl}/k_{MA})[Cl_2]$, whence the ratio of the rate constants may be found. From Figure 9 the value of $(k_{Cl}/k_{MA})[Cl_2]$ is equal to 1.6, and that of (k_{Cl}/k_{MA}) is equal to 2.91.

Upon chlorocarboxylation of PIB, the radical accepting effect of MA is observed. In the presence of MA the rate of PIB chlorination decreases, as it is seen in Figure 4.

Table 1. The values of rate constant of PIB chlorination reaction in the presence of MA.

$[Cl_2]_0$ (mol/L)	$[PIB]_0$ (mol/L)	$[PIB]_0$ (mol/$L^{1/2}$)	$[MA]_0$ (mol/L)	$V_0 \cdot 10^5$ (mol/L)	$K \times 10^5$ ($L^{1/2}$/ $mol^{1/2}$.s)
0.550	0.357	0.597	0.03	11.75	35.78
0.550	0.357	0.597	0.05	11.90	36.24
0.545	0.357	0.597	0.01	11.70	35.91
0.445	0.373	0.611	0.022	8.90	32.73
0.557	0.357	0.597	0.024	11.80	35.49
0.648	0.389	0.624	0.021	13.30	32.89
0.322	0.178	0.422	0.018	4.05	29.80
0.320	0.357	0.597	0.018	5.83	30.52
0.350	0.782	0.884	0.018	9.09	29.38

To explain this phenomenon, the particularities of the process mechanism should be taken into consideration. In the chlorocarboxylation process of PIB, the formation of the macroradical takes place:

$$\begin{array}{ccc}
CH_3 & & \overset{\cdot}{C}H_2 \\
| & +Cl_2 & | \\
-CH_2-C- & \xrightarrow{\quad h\nu \quad} & -CH_2-C- + HCl \\
| & & | \\
CH_3 & & CH_3
\end{array} \qquad (8)$$

The radical (I) adds a chlorine atom or MA molecule. The availability of MA in the reaction medium significantly influences the course of the chlorination reaction.

This is shown in Figure 10. It is evident from this figure that the value of N_{OCl} (a number of the sites in the PIB chain occupied by chlorine upon chlorination without MA) always exceeds the sum value (N_{Cl} + N_{MA}):

$$N_{OCl} > (N_{Cl} + N_{MA}) \qquad (9)$$

Such a deviation may be explained by accepting the action of MA which, according to [10, 11], occurs in the case of chlorocarboxylation of polyethylene. This

Table 2. The portions of the chlorinated and carboxylated sites of CCPIB chain.

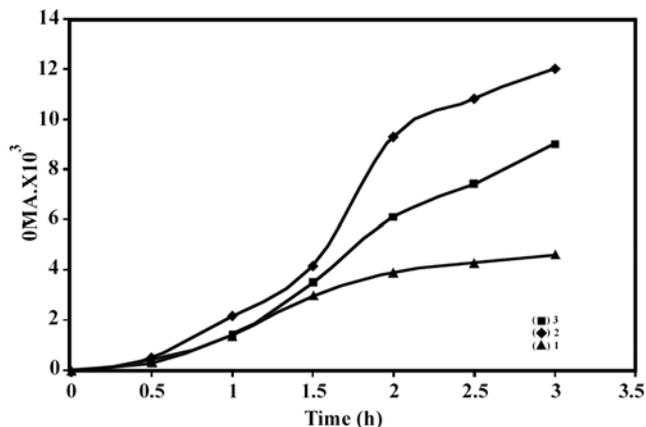| Time (h)	Chlorine content in CCPIB (%)	MA Content in CCPIB (%)	θ_{Cl}	$\theta_{MA} * 10^3$	$\ln\theta_{MAo}/(\theta_{MAo}-\theta_{Mat})$
$[Cl_2]_0 = 0.55$ mol/L; $[MA]_0 = 0.01$ mol/L; $[PIB]_0 = 0.357$ mol/L					
0.5	7.0	0.15	0.031	0.26	0.029
1.0	28.0	0.7	0.162	1.593	0.189
1.5	51.0	0.95	0.432	3.17	0.416
2.0	52.5	1.10	0.463	3.814	0.525
2.5	53.0	1.25	0.472	4.390	0.640
3.0	55.0	1.30	0.512	4.770	0.719
$[Cl_2]_0 = 0.55$ mol/L; $[MA]_0 = 0.03$ mol/L; $[PIB]_0 = 0.357$ mol/L					
0.5	4.0	0.2	0.017	0.34	0.0108
1.0	14.0	0.85	0.068	1.63	0.0590
1.5	42.0	1.30	0.305	3.72	0.1410
2.0	50.0	1.90	0.440	6.51	0.2640
2.5	51.5	2.15	0.460	7.57	0.3160
3.0	53.0	2.50	0.492	9.18	0.3980
$[Cl_2]_0 = 0.55$ mol/L; $[MA]_0 = 0.05$ mol/L; $[PIB]_0 = 0.357$ mol/L					
0.5	3.0	0.30	0.128	0.50	0.0108
1.0	12.1	1.20	0.058	2.27	0.0497
1.5	28.0	1.90	0.166	4.45	0.0952
2.0	47.0	2.85	0.390	9.36	0.2238
2.5	48.5	3.10	0.420	10.60	0.2576
3.0	50.0	3.40	0.465	12.30	0.3057

Figure 7. The curves of θ_{MA} change versus the PIB chloro-carboxylation time. The mass ratio PIB:MA; (1)-100:5, (2) 100:15, (3) 100:25.
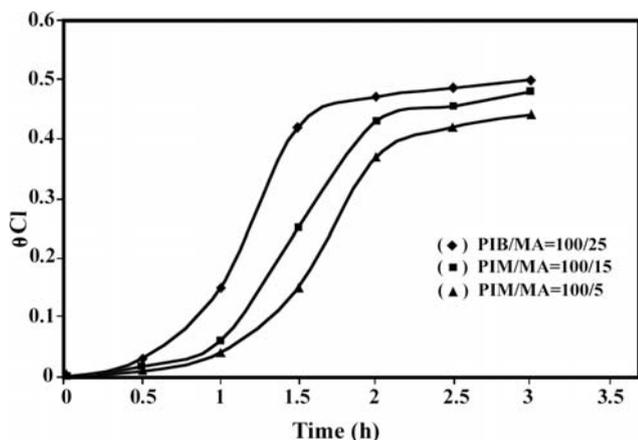

Figure 8. The curves of θ_{Cl} change versus the PIB chlorocar-boxylation time.
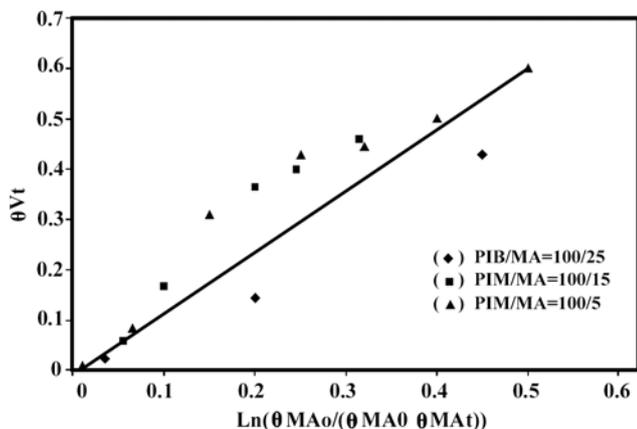

Figure 9. Dependency of θ_{Cl} on $\theta_{MAo}/(\theta_{MAo}-\theta_{Mat})$ in the process of PIB chlorocarboxylation.

accepting effect in the case of PIB should be attributed to the typical one because of the sufficiently high con-
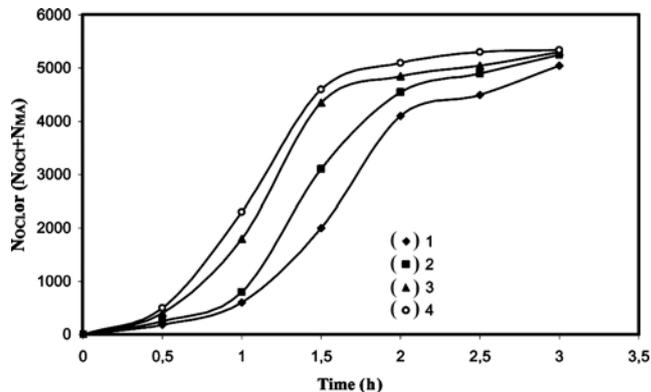

Figure 10. N_{ocl}.or $(N_{ocl}+N_{MA})$ as a function of time. (1)-chlorocarboxylation of PIB at the mass ratio PIB:MA=100:25, (2)-chlorocarboxylation of PIB at the mass ratio PIB:MA=100:15, (3)-chlorocarboxylation of PIB at the mass ratio PIB:MA=100:5, (4)-chlorination of PIB.
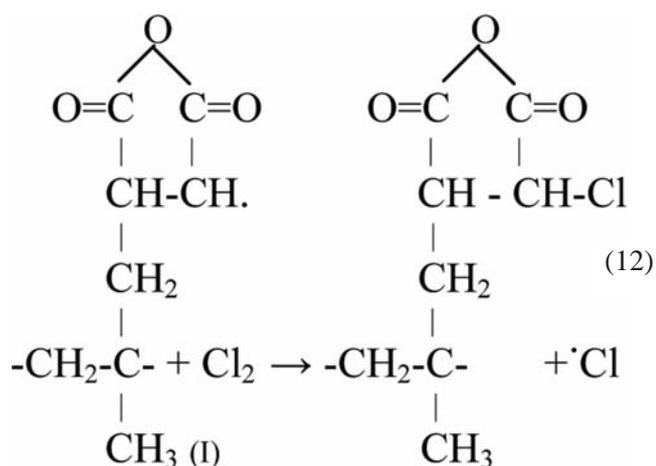
centration of MA in the reaction medium. The decrease of PIB chlorination rate in the presence of MA may be probably elicited by occurrence of the following reaction (scavenging):
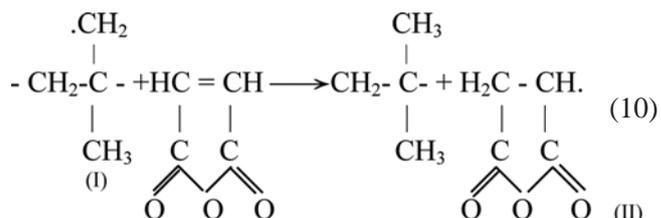
In the process of PIB chlorocarboxylation, the macroradical (I) can also react with MA forming the macroradical (III):
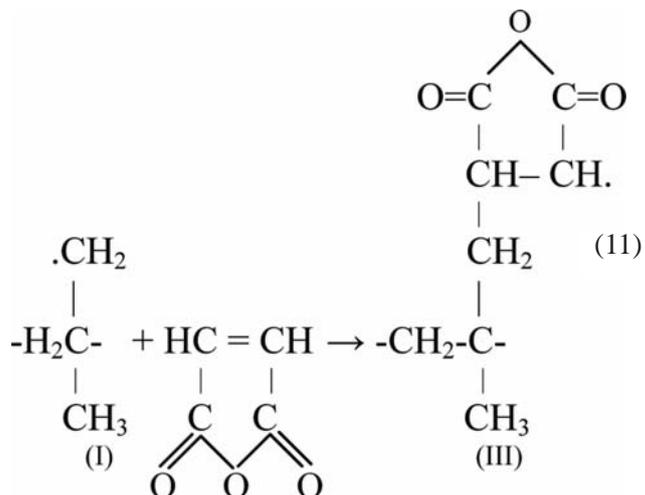
The macroradical (III) may also be deactivated by chlorine:

$$(12)$$

The formed Cl radicals may generate formation of the macroradicals (I).

The numbers of sites in the chain of PIB occupied by chlorine and MA are taken into account in the study of kinetics of MA accepting effect (scavenging). The analysis was made by comparing the rates of PIB chlorination in the absence and presence of MA under identical conditions.

The above given relationship numbered (9) may be written as:

$$N_{SCV} = N_{OCl} - (N_{Cl} + N_{MA}) \qquad (13)$$

where N_{SCV} is the number of the sites undergone scavenging. The portion of the chain sites where scavenging takes place (θ_{SCV}) may be ascertained by the equation:

$$\theta_{SCV} = (N_{0Cl} - (N_{Cl} + N_{MA}))/N_{0Cl} \qquad (14)$$

The characteristics of MA scavenging process upon chlorocarboxylation of PIB is given in Table 3.

The curves θ_{SCV} versus time (Figure 11) have a particular shape and reflect the total influence of all the peculiarities of the process. In the process of PIB chlorocarboxylation, after some extent of substitution, the effect of neighbouring groups begins to play an important role and the rate of radical scavenging decreases. The neighbouring group effect also causes a decrease in the rates of substitution by chlorine and

Table 3. Characteristics of the scavenging effect of MA upon chlorination of PIB.

Time (h)	N_{OCL}	N_{Cl}	N_{MA}	$(N_{Cl}+N_{MA})$	$\theta_{SCV} = (N_{0CV}(N_{Cl}+N_{MA}))/N_{0CV}$	MA (concentration, mol/L)
0.5	444.51	144.4	5.71	150.1	0.662	0.05
1.0	2361.53	652.6	25.52	67.81	0.713	---
1.5	5000.14	1870.4	50.15	1920.5	0.616	---
2.0	5500.25	4397.9	105.34	4503.2	0.181	---
2.5	5824.21	4726.9	119.23	4846.1	0.168	---
3.0	5939.52	5231.5	138.47	5369.9	0.096	0.05
0.5	444.5	194.6	3.83	198.4	0.554	0.03
1.0	2361.53	765.9	18.34	784.2	0.668	---
1.5	5000.14	3426.7	41.82	3468.5	0.306	---
2.0	5500.25	4959.0	73.28	5032.3	0.087	---
2.5	5824.21	5173.6	85.12	5258.7	0.097	---
3.0	5939.52	5537.8	103.22	5641.0	0.052	---
0.5	444.5	350.1	2.96	353.04	0.206	0.01
1.0	2361.53	1817.9	17.92	1835.91	0.223	---
1.5	5000.14	4856.5	35.67	4892.14	0.022	---
2.0	5500.25	5203.8	42.91	5246.73	0.046	---
2.5	5824.21	5305.3	49.37	5354.75	0.081	---
3.0	5939.52	5759.3	53.71	5813.04	0.021	---

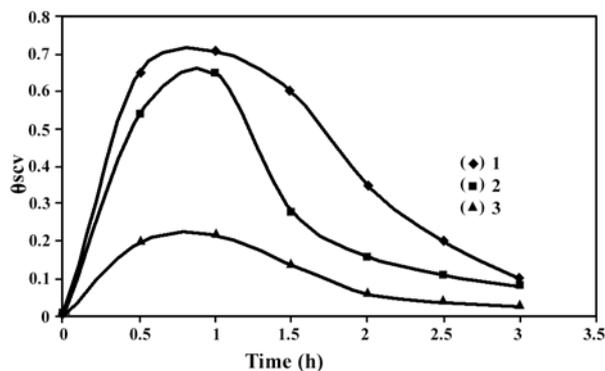**Figure 11.** θ_{SCV} as a function of PIB chlorocarboxylation time. (The mass ratio PIB:MA, (1) 100: 25, (2) 100:15, (3) 100:5).

MA. For an effective collision with PIB macroradical, voluminous MA molecules must overcome considerable steric barriers. Meanwhile, more active and mobile chlorine molecules retain possibilities to attack the PIB chain. As a result, in the course of the reaction, the scavenging effect passes through maximum, and then decreases in such a manner that, in the product of PIB chlorocarboxylation, further, predominantly chlorination occurs. The observed effect is illustrated in Figure 11. The maximum scavenging effect, according to the obtained experimental data, is observed after about 1 h since the beginning of the process.

CONCLUSION

In this study, photochemical chlorination of polyisobutylene was performed in the presence of chlorine solution in CCl_4 and maleic anhydride in $CHCl_3$. Chlorocarboxylation was achieved together with chlorination. The ratio of the rate constant of chlorination reaction to the rate constant of chlorocarboxylation reaction was found to be equal to 291.

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