

A STUDY ON THE DEGRADATION MECHANISM OF PHOTOCROSSLINKING PRODUCTS FORMED BY CYCLIZED POLYISOPRENE-DIAZIDE SYSTEM UNDER THE INFLUENCE OF ALKYL BENZENE SULFONIC ACIDS

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ABSTRACT

The degradation mechanism of photocrosslinking products formed by cyclized polyisoprene-diazide system under the influence of the different alkyl benzene sulfonic acids was studied. The effects of alkyl chain length and the concentration of alkyl benzene sulfonic acids on the rate of degradation reaction were discussed. It was found that in the initial stage of degradation, the cyclicity ratio and the average fused ring number did not change considerably, but the percentage of uncyclized parts content varied significantly. The suitable mechanism was supposed.

INTRODUCTION

The photosensitive polymer such as cyclized polyisoprene-diazide system has been widely used in the manufacture of semiconductor parts and printing industry. The photochemical reaction mechanism of this system was studied by many authors^[1-3], but how to remove the unsolved and unmelted photocrosslinked polymer after completing the mission to resist the etching of chemicals is a very important and still unresolved problem in microfabrication.

We have reported that the three dimensional networks of photocrosslinked products of cyclized polyisoprene-diazide system might be broken, degraded and dissolved in the halogenated alkene under the influence of alkyl benzene sulfonic acids^[4]. But the degradation process has not yet been made clear up to now.

In the further research it was found that the degradation rate was raised with the increase of the concentration of alkyl benzene sulfonic acids and the chain length of alkyl groups. In the initial stage of the degradation, the cyclicity ratio and average fused ring number did not change considerably, but the percentage of uncyclized parts content varied significantly. Therefore it is not only broken at the crosslinking points of the crosslinked networks, but also the uncyclized parts might be cut off from the crosslinked polyisoprene under the influence of alkyl benzene sulfonic acids.

The measured results of activation energy confirmed that the dodecyl benzene sulfonic acid is the best catalyst for degradation of photocrosslinked products formed by cyclized polyisoprene-diazide system.

EXPERIMENTAL PART

Preparation of photocrosslinked sample

The preparation method of photocrosslinking sample of cyclized polyisoprene - diazide system is carried out as we have reported^[4].

Degradation process

A certain weight of the photocrosslinking sample was added to the mixed solution consisting of alkyl (R) benzene sulfonic acid and tetrachloroethylene (weight ratio: 1/3, R: methyl (I), ethyl (II), isopropyl (III) from Shanghai First Reagent Plant, A. R.; R: dodecyl (IV) from Nan Jing Petroleum Factory), then the mixed solution was stirred at 80 °C for definite time under nitrogen. An excess of methanol (3:1 by volume of the mixed solution) was added to the solution, stand for 1h and then filtered. The precipitate was washed with 95% alcohol till the pH₁ of the filtrate to 7 (the filtrate was kept for separation by TLC), then it was vacuum dried to constant weight.

Cyclization of linear polyisoprene

To natural rubber ($\overline{M}_n = 1 \times 10^6$, No. 1 of Hei Nan, China) xylene solution (concentration: 5%) p-toluene sulfonic acid (5.6% of rubber weight) was added, it was reacted to cyclize in the solution for 8h at 138 °C under nitrogen. Then another part of natural rubber xylene solution with the same concentration and volume like the former was added to the above-mentioned solution. The mixed solution was ceased to react by triethyl amine at different cyclized time. Methanol was used as a precipitant, the precipitate was washed, dried for measurement.

Separation of the residue in the degradation by TLC

The filtrate formed in the degradation process was concentrated for TLC (absorbent: E. Merck Silica Gel 60H, adhesion agent: CMC). Mixed solvents (benzene: chloroform (v/v) = 90:10) were used as developing agent.

The bands of $R_f = 0.14, 0.37$ and 0.64 were cut off from the TLC plant.

Identification of the separated products from the residue

The separated product of $R_f = 0.64$ was orange powder, m. p.: 98 ~ 101 °C.

Elementary analysis: $C_{20}H_{20}N_2O$ (calcd: C 78.95, H 6.58, N 9.21; found: C 78.66, H 6.79, N 9.02);

IR: (KBr) (CCl_4) 3377, 3305 (NH, double peak), 1664 (α, β unsaturated C=O), 1620 (C=C conjugated with phenyl ring), 1321 (C-N), 824 (1, 4-disubstituted phenyl ring) cm^{-1} ;

MS: m/e 304 (M^+), 276 ($M^+ - CO$), 246 ($M^+ - CO, -NH_2\dot{C}H_2$), 152 ($M^+ - CO, -2NH_2\dot{C}H_2, -C_5H_4$);

^1H NMR ($CDCl_3$) (TMS): 1.5 ~ 2.8 (6 H, m, $-CH_2-$), 3.3 (4H, s, $-NH_2$), 6.2 ~ 7.14 (10H, m, $-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-$) ppm.

The structures of the separated products of $R_f = 0.14, 0.37$ are still unclear.

Instrumentation

IR was recorded on Perkin–Elmer 983G spectrometer ;

MS was measured on FINNIGAN MAT 4510 GC/MS;

^1H NMR was performed on Bruker Co. MSL–300 NMR spectrometer, TMS was used as internal standard .

RESULTS AND DISCUSSION

1. The reaction order and rate constants of degradation reaction

Fig. 1 represents a plot of natural logarithm to the base of weight difference between original photocrosslinking sample (W_0) and insoluble part (W) after degradation over W_0 against reaction time, the linear relationship between them could be found. Therefore the degradation process of photocrosslinking products formed by polyisoprene– diazide system under the influence of alkyl benzene sulfonic acids is a first order reaction.

The rate constants of degradation reaction at 80°C could be obtained from the slope of straight lines in Fig. 1, its values are 0.010, 0.013, 0.023 and 0.175 s^{-1} respectively for alkyl benzene sulfonic acids (I), (II), (III) and (IV).

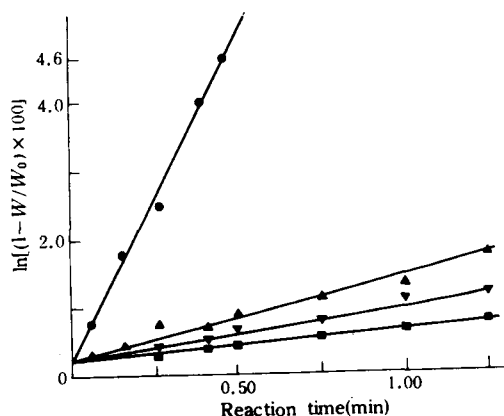


Fig.1 The effect of reaction times on the degradating rate of photocrosslinking products. (Temp.: 80°C , the concentration of alkyl benzene sulfonic acids: 15%, solvent: tetrachloroethylene) alkyl benzene sulfonic acids (R): ● dodecyl, ▲ isopropyl, ▼ ethyl, ■ methyl.

2. Activation energy of degradation reaction

A series of rate constants of degradation reaction could be measured by variation of temperature as indicated in Table 1. According to Arrhenius formula, the activation energy of degradation could be derived by a plot of $\ln k$ as a function of reciprocal of reaction temperature.

For different alkyl benzene sulfonic acids (I), (II), (III) and (IV), their values are 30.60, 30.54, 29.23 and $16.50\text{ kcal mol}^{-1}$ respectively (Fig. 2).

Table 1 The degradation rate constants at different temperature *

$k \times 10^4 (s^{-1})$ / $R-\text{C}_6\text{H}_4-\text{SO}_3\text{H}$	$\text{CH}_3-\text{C}_6\text{H}_4-\text{SO}_3\text{H}$	$\text{C}_2\text{H}_5-\text{C}_6\text{H}_4-\text{SO}_3\text{H}$	$\text{CH}_3-\text{CH}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{SO}_3\text{H}$	$\text{CH}_3-(\text{CH}_2)_{11}-\text{C}_6\text{H}_4-\text{SO}_3\text{H}$
Temp. (°C)				
20	0.013	0.018	0.045	14.000
40	0.368	0.507	1.098	84.963
60	7.135	9.742	18.593	378.570
80	100.010	133.104	227.000	1750.000
100 **	537.000	341.000	656.000	2159.000

* Photocrosslinking product 1.5 g was reacted with 10 ml alkyl benzene sulfonic acids (concentration: 15%).

** The k values at 100 °C are deviated from the normal because the tetrachloroethylene is partly volatilized at this temperature.

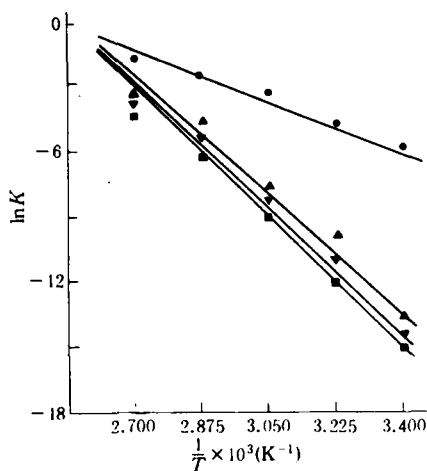


Fig. 2 The relationship between $\ln k$ and the reaction temperature.

alkyl benzene sulfonic acids (R):

● dodecyl, ▲ isopropyl,
▼ ethyl, ■ methyl.

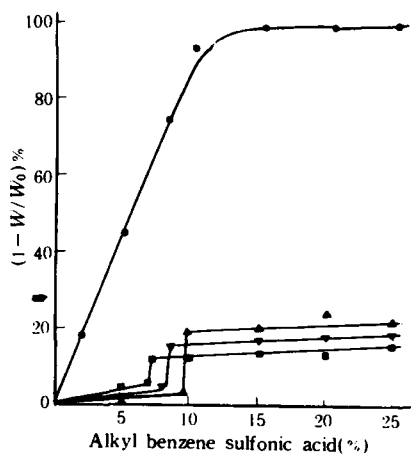


Fig. 3 The effect of the concentrations of alkyl benzene sulfonic acids on the degrading rate.

(reaction time : 30 s, temp: 80 °C)

alkyl benzene sulfonic acids (R):

● dodecyl, ▲ isopropyl,
▼ ethyl, ■ methyl.

3. Effect of the concentration of alkyl benzene sulfonic acids on the degradation rate

The curves in Fig. 3 were obtained by a plot of contents percentage of degradation products against the concentration of alkyl benzene sulfonic acids. Fig. 3 indicated that the contents percentage of degrading products were increased with the increment of the contents of dodecyl benzene sulfonic acid in tetrachloroethylene. The maximum of degrading rate appeared when the concentration of dodecyl benzene sulfonic acid reached 15%. The degrading rate was not changed obviously when the concentration of latter increased further.

For alkyl benzene sulfonic acids with short chain (I), (II) and (III), only when the concentration appeared to 8 ~ 10% can the degradation products be detected. The variation of the degradating rate approached to constant when the concentration of alkyl benzene sulfonic acids (I), (II) and (III) was raised further.

The above-mentioned experimental facts were attributed to the different solubilizing behaviors of alkyl benzene sulfonic acids with different chain length for cyclized polyisoprene which was broken from the crosslinking points in the presence of $H^{+[5]}$.

4. ^1H NMR analysis of chain structure of degradating products

In order to grasp the essentials of the degradation reaction, the chain structure of the degradating products which was formed at the different reaction times under the influence of dodecyl benzene sulfonic acid were analyzed by ^1H NMR. It was found that in the initial stage of the degradation reaction, the variation of cyclicity ratio and average fused ring number was not changed obviously, but the percent of uncyclized parts contents of the system was varied significantly. For example, Table 2 showed that having reacted 10 min at 40 °C, the percent of uncyclized parts contents was varied from 42% to 27%, but the cyclicity ratio was changed from 0.254 to 0.258, and the average fused ring number from 2.1 to 2.2 only. Therefore not only should be broken at the crosslinking points of the photocrosslinking products, but also the uncyclized parts of the latter might be cut off from the crosslinking network under the influence of dodecyl benzene sulfonic acid. If it was broken at the crosslinking points only, the chain structure of the degradation products should be similar to the linear cyclized polyisoprene in which the average fused ring number was increased with the consumption of uncyclized parts in chain segments. But when the uncyclized parts were cut off from the end or two ends of cyclized polyisoprene, the average fused ring number did not raise with the decrement of the contents percent of uncyclized parts in the first period of the degradating till the value approached or equaled to the average fused ring number of the original system.

As a comparison, the linear polyisoprene was added to the xylene solution of polyisoprene which has reacted to be cyclized for 8 hs (toluene sulfonic acid was used as a catalyst) at 138 °C, the average fused ring number and the contents percent of uncyclized parts at the different reaction times and temperatures were measured. The results indicated that as soon as the linear polyisoprene was added to the cyclized system the average fused ring number of mixed solution was decreased at first due to the increment of the linear polyisoprene. Having reacted for 3 hs, the average contents of double bonds of the system varied greatly, but the average fused ring number did not vary obviously as Table 3.

It was confirmed that the main reaction of the mixed solution during this period was the cyclization of linear polyisoprene, only the average fused ring number of the latter reached to the average value of original cyclized system approximately after reacting for 6hs the increment of this value became more distinct.

When the average fused ring number reached to 3, it was no longer varied with the variation of the reaction times and temperature. Probably the reason is that when the average fused ring number was more than 3, the chain became too rigid to be cyclized further.

Table 2 ^1H NMR analysis of the degrading products

Reaction temp. (°C)	Reaction times (min.)	Square of proton peaks				Total Square	Contents of uncyclized part (P)	Cyclicity ratio (Q) [6]	Average fused ring number (n) [7]
		Cyclized parts	uncyclized parts						
		$\text{CH}_3 - \underset{\text{(E)}}{\underset{ }{\text{C}}} - \text{CH}_2 <$		$\text{CH}_3 - \underset{\text{(B)}}{\underset{ }{\text{C}}} = \text{CH} =$		(c)	$P = \frac{8B}{\varepsilon} 100\%$	$Q = \frac{E}{\varepsilon - 8B}$	$n = \frac{8Q}{3 - 8Q}$
		$\delta = 0.86 \sim 1.01$	$\delta = 4.60$	$\delta = 1.60$	$\delta = 5.12$				
40	0.08	8.78	3.98	8.76	3.13	59.62	42	0.254	2.1
	1.00	6.89	3.12	5.82	2.08	43.79	38	0.154	2.1
	5.00	8.30	3.76	5.54	1.98	48.80	33	0.258	2.2
	10.00	12.50	5.67	6.27	2.24	66.37	27	0.258	2.2
	30.00	10.23	4.64	4.67	1.67	55.67	24	0.271	2.6
	45.00	11.40	5.17	4.00	1.43	52.00	22	0.281	3.0
	60.00	14.46	6.55	4.70	1.68	64.00	21	0.286	3.2
	120.00	10.42	4.72	3.39	1.21	46.10	21	0.286	3.2
80	0.08	8.72	3.95	8.00	2.86	57.18	40	0.254	2.1
	1.00	9.51	4.31	8.45	3.02	62.04	39	0.251	2.0
	5.00	8.76	3.97	5.37	1.92	49.57	31	0.256	2.1
	10.00	12.75	5.78	5.62	2.01	64.19	25	0.265	2.4
	30.00	14.03	6.36	5.03	1.80	65.62	22	0.274	2.7
	45.00	11.23	5.09	3.69	1.32	50.24	21	0.284	3.1
	60.00	10.85	4.92	3.30	1.18	47.38	20	0.286	3.2
	120.00	10.18	4.62	3.28	1.18	44.95	21	0.286	3.2

Table 3 ^1H NMR measurement of cyclized polyisoprene **

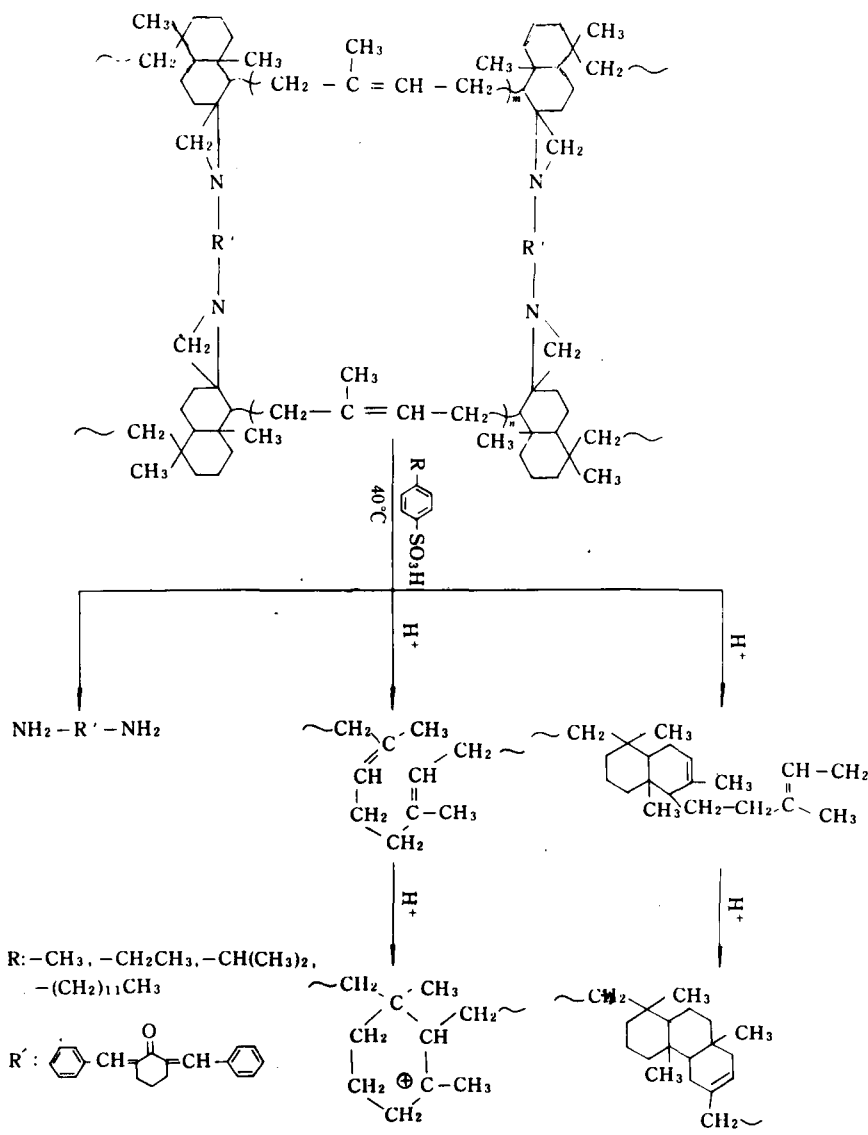
Sample No	Reaction times (hr.)	Square of proton peaks				Total square	Contents of uncyclized part (P)	Cyclicity ratio (Q) [6]	Average fused ring number (n) [7]
		Cyclized parts	uncyclized parts						
		$\text{CH}_3 - \underset{\text{(E)}}{\underset{ }{\text{C}}} - \text{CH}_2 <$		$\text{CH}_3 - \underset{\text{(B)}}{\underset{ }{\text{C}}} = \text{CH} =$		(c)	$P = \frac{8B}{\varepsilon} 100\%$	$Q = \frac{E}{\varepsilon - 8B}$	$n = \frac{8Q}{3 - 8Q}$
		$\delta = 0.86 \sim 1.01$	$\delta = 4.60$	$\delta = 1.60$	$\delta = 5.12$				
1	8	7.55	3.42	7.53	2.69	52.85	40	0.241	1.8
2	1	5.34	2.87	12.46	4.45	64.16	55	0.187	1.0
	3	9.04	4.09	9.13	3.26	67.35	39	0.219	1.4
	6	10.41	4.72	6.75	2.41	52.87	36	0.245	1.9
	8	8.23	3.73	3.58	1.28	40.96	25	0.268	2.4
	10	9.51	4.31	2.83	1.01	42.53	19	0.276	2.8

** Sample 1 was prepared from a part of xylene solution of polyisoprene (conc: 5%, p-toluene sulfonic acid was used as a catalyst) which has been cyclized for 8 hrs at 138 °C. This part of solution was ceased to react by triethylamine, then was precipitated by methanol, the precipitate was washed, dried for measurement.

Sample 2 was obtained by the procedure like that: the linear polyisoprene (conc: 5%) was added to above-mentioned solution which was cyclized for 8 hrs, the mixing reactant at the different cyclized times was treated as sample 1.

5. The degradation mechanism

On the basis of above experimental results and discussion, and the 2,6-bis(4'-aminobenzal) cyclohexanone was separated from the degrading products by TLC, the degradation mechanism of photocrosslinking products formed by cyclized-diazide system under the influence of alkyl sulfonic acids might be as follows:



Keywords :

cyclized polyisoprene; diazidocompounds; photocrosslink; alkyl benzene sulfonic acid; degradation.

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