Polymer Bulletin 5, 463–468 (1981)

Polymer Bulletin

Reaction of Poly(epichlorohydrin) with Sodium Diethyldithiocarbamate and RI-UV Dual-Detector GPC of the Product

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Summary

The chlorine in poly(epichlorohydrin) was found to be substituted by diethyldithiocarbamate (ETC) group by the reaction with NaETC in tetrahydrofuran at 60°C. The reaction product was analyzed by RI-UV dual-detector GPC. The composition i.e. the percentage of the chlorine replaced by the ETC group was found to be invariant with the elution count. This result might indicate the absence of polymer effect in the carbamation of poly(epichlorohydrin).

Introduction

Recently the utility of dual-detector GPC has been noted (CAZES and DELAMARE 1980), and several studies on copolymer compositions by this method have appeared (ADAMS 1971, MORI 1978 and 1980, WALCHLI et al. 1978, TERAMACHI et al. 1978). Poly(epichlorohydrin) is commercially available as chlorohydrin rubber (CHR). This communication concerns a functionalization of CHR by the polymer reaction with sodium diethyldithiocarbamate (NaETC) and the RI-UV dual-detector GPC analysis of the product. The chemical utilization of this functionalized CHR (ETC-CHR) will be given in a forthcoming publication (YAMASHITA et al.).

Experimental

The reaction of CHR with NaETC was carried out in tetrahydrafuran (THF) at 60°C under a nitrogen atmosphere. The product was coagulated by methanol and purified by the reprecipitation (THF/methanol). A Knauer membrane osmometer

0170-0839/81/0005/0463/$01.20

was used to determine the number-average molecular weights. The GPC apparatus used in the present study was a high-speed liquid-chromatography HLC-802 (Toyo Soda Manufacturing Co., Ltd) equipped with a differential refractometer (RI) and an ultraviolet (254 nm) detector (UV). The column set was composed of four columns of TSK-GELs (G2000H8 x 2, G3000H8, and G4000H8) having length of 2 ft, respectively. The eluent was THF, the flow rate 1.0 ml/min, and the column temperature was maintained at 40°C. The calculation of composition from RI and UV responces was reported by Teramachi et al. (1978). All materials were purified by the standard methods.

Results and Discussion

Carbamation of CHR

Carbamate groups are known to produce free radicals under an ultraviolet or visible light irradiation, hence they are photo-sensitive groups (OKAWARA et al. 1963 and 1970). We, therefore, attemped the carbamation of CHR. Carbamations of chloromethylated polystyrene (OKAWARA et al. 1963), poly(vinyl chloride)(OKAWARA et al. 1966, NAKAGAWA et al. 1971), and chlorinated poly(ethylene)(NAKAGAWA and YAMADA 1972) were published, and a patent literature (MARKLOW 1966) described the carbamation of oligomeric poly(epichlorohydrin). Carbamation of 1-chlorobutadiene copolymers was also studied by us (HONGU et al. 1977, YAMASHITA et al. 1977). Having taken all these results into account and carried out an extensive experiment, we found this nucleophilic substitution reaction on CHR was possible in THF at 60°C with NaETC.

Some results are shown in Table 1. ^{1}H NMR of the product (No. 7) in $CDCl_3$ showed two peaks: δ 1.27 (triplet, CH_3 in ETC); δ 3.70 (broad singlet, CH_2s in ETC and CHR, and CH in CHR). The relative peak-area ratio was in conformity with the [ETC] from UV spectroscopy. Because ETC group in ETC-CHR showed absorption maximum in UV region (λ_{max} 280 nm in THF), the ETC group could be assayed using ε_{max} = 9,200. This value was taken from the UV spectrum of N,N-diethyl-S(2-oxabutyl)-dithiocarbamate (EOC) (λ_{max} 282 nm and ε_{max} = 9,200

TABLE 1

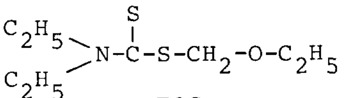
Reaction of CHR with NaETC in THF at 60°C

No.	[CHR] (g/l)	[NaETC] (g/l)	[ETC]/[Cl][a]	Reaction time (h)	[ETC][b] (mole %)
1	30.0	7.2	0.100	1.5	0.44
2	"	"	"	6.0	1.41
3	"	"	"	12.0	2.48
4	"	"	"	24.0	4.54
5	44.0	53.0	0.346	3.0	4.83
6	"	"	"	6.0	9.68
7	"	"	"	16.0	26.6
8	33.0	40.0	0.505	3.0	5.43

[a] Molar ratio of [ETC] to [Cl] of CHR in the feed.

[b] Mole % of the chlorine replaced by ETC group, which is determined by UV spectroscopy.

in THF), which was synthesized from chloromethyl ethyl ether and NaETC. The synthesized EOC was



EOC

analyzed by elemental analysis (Found: C, 46.67; H, 8.52; N, 6.97; S, 30.97 %. Calculated: C, 46.34; H, 8.26; N, 6.76; S, 32.92 %), and by ^{1}H NMR in $CDCl_3$: δ 1.0-1.4 (multiplet, three CH_3s); δ 3.6 (quartet, CH_2 in C_2H_5O-); δ 3.9 (broad, two CH_2s in C_2H_5N-); δ 5.5 (singlet, CH_2 in -O-CH_2-S-) with relative area ratio of 9:2:4:2 which was in full conformity with the calculated. We assume this compound can be a model of the ETC unit in ETC-CHR. The ETC contents thus determined by UV spectroscopy are listed in the 5th column in Table 1. They are in good agreement with those by elemental analysis; for example, No. 5 4.59 mole % from S (%) and 4.90 mole % from N (%) and No. 8 5.10 mole % from S (%) and 5.83 mole % from Cl (%).

From the results in Table 1 it was found that the nucleophilic substitution reaction of chlorine in CHR by NaETC is possible under relatively mild conditions. The other product i.e. NaCl and the unreacted NaETC could be removed easily by reprecipitation. Molecular weight measurements of CHR and

ETC-CHR No. 6 by a membrane osmometer showed 2.20 x 10^5 and 2.97 x 10^5, respectively. These values indicate that degrees of polymerization of the two polymers were almost identical. Therefore, the degradation of CHR was improbable under the present reaction conditions. The calculated molecular weight of No. 6 from its ETC group content was 2.46 x 10^5, which is a little smaller than the experimental value. The reaction product, ETC-CHR, was subject to reprecipitations for its purification, and some low molecular-weight polymers were lost during the processes.

RI-UV GPC of ETC-CHR

Because ETC group was highly UV-sensitive as described earlier, we started the study of ETC-CHR by RI-UV dual-detector GPC to elucidate the relationship between the molecular weight and the composition in polymer reactions. In Figure 1 is shown the result on ETC-CHR No. 8 (Table 1).

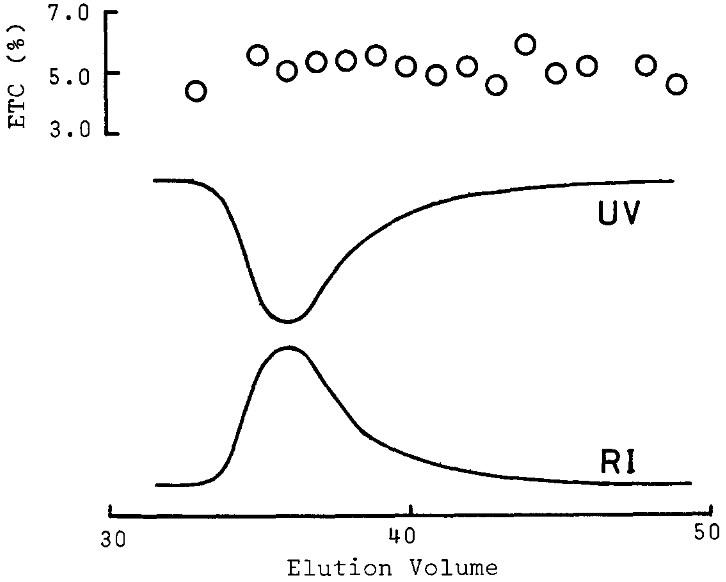


Fig. 1 UV-RI dual-detector GPC of ETC-CHR

Sample: No. 8 in Table 1. ETC(%) is the percentage of chlorine substituted by ETC group.

Here, the polymer had been fractionated by GPC, and the RI responce was proportional to the amount of the polymers, the UV responce to that of ETC group in the polymers excluded at each elution count. The ETC content in ETC-CHR remains constant at all elution counts. In other words, the products of the polymer reaction between CHR and NaETC contain equal amount of ETC group regardless of their molecular weights. This result can be interpreted by the absence of polymer effect in the carbamation of CHR, i.e., the substitution takes place randomly on the CHR polymer chains and the length of the chain has no effect on the reaction. This finding presents a clear contrast with the reported polymer effect on the carbamation of poly(vinyl chloride) in dimethylformamide (OKAWARA et al. 1966).

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Received September 9, 1981
Accepted September 29, 1981

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