Polymer Bulletin 6, 209–215 (1981)

Polymer Bulletin

Chemical Determination of Microstructure of Diene Units in 1-Chloro-1,3-Butadiene Copolymers

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Summary

Microstructure of 1-chloro-1,3-butadiene (CB) units in the copolymers with styrene and with 1,3-butadiene was elucidated by chemical reactions. The reactivities of the two chlorines, i.e., that of 1,4-microstructure CB units and that of 3,4-microstructure, were drastically different from each other in the substitution by diethyldithiocarbamate group as well as in the hydrogen chloride elimination during thermogravimetric measurements. This difference enabled us to determine the microstructure of CB units in poly(CB-co-styrene) and poly(CB-co-1,3-butadiene). The results showed ca. 60 percent of CB units was of 1,4-microstructure and the rest was of 3,4-microstructure. These results were in good agreement with those by spectroscopies.

Introduction

Microstructure of diene units in poly(diene) is usually elucidated by infrared and NMR spectroscopies (BOVEY 1972, VER STRATE 1978, KOHJIYA et al. 1981). Before the advent of convenient spectroscopic instruments, the microstructure was determined by chemical reactions. For example, ozonolysis of poly(diene) followed by analysis of the product gave informations on the microstructure of diene units (MOCHEL & NICHOLS 1951, BARNARD 1956). The chemical reactions used for such determinations have to be quantitative. Thus, many reactions which can be applied to the qualitative purposes were excluded.

This paper describes the microstructure determinations

0170-0839/81/0006/0209/$01.40

of 1-chloro-1,3-butadiene (CB) units in CB polymers by the reactions with sodium diethyldithiocarbamate (NaETC) and by the thermal dehydrochlorination. These methods would be of much value to the microstructure determination of CB units in poly(CB-co-1,3-butadiene). Spectroscopies do not give clear-cut results for this copolymer, because the chemical structures of the two monomer units were very similar (KOHJIYA et al. 1981).

Experimental

CB was synthesized as reported (HEASLEY and LAIS 1968). All the materials were used after pertinent purifications. The copolymerization of CB with styrene or with 1,3-butadiene (Bu) was carried out in bulk at 70°C in the presence of 2,2'-azobis(isobutyronitrile). All the copolymers were obtained at low conversions and their compositions (CB contents) were determined from elemental analysis of chlorine. The reactions of polymers with NaETC were conducted in dimethylformamide (DMF) or in a binary mixture of DMF and tetrahydrofuran (THF) (3:5 in volume ratio) at 50°C under nitrogen. The initial concentration of NaETC was twice that of total chlorine in the polymer, and the polymer concentration was 10.0 g/l. The product was purified by reprecipitation, and its ETC-group concentration was determined by elemental analysis and/or UV spectroscopy ($\lambda_{max's}$ = 254 and 281 nm, $\varepsilon_{max's}$ = 11000 and 11500, respectively). These extinction coefficients were the values for 2-butenyl N,N-dimethyldithiocarbamate, which was synthesized from 1-chloro-2-butene (trans isomer). We assumed 1-chloro-2-butene could be a model compound for the 1,4-microstructural CB unit. In facts, the ETC concentrations by UV method agreed well with those by elemental analysis. Thermogravimetry (TG) was conducted with a Rigaku TG Instrument (Japan) under an air stream of 20 ml/min. The rate of temperature increase was 10°C/min.

Results and Discussion

Carbamation of Poly(CB-co-Styrene)

The analytical results on poly(CB-co-styrene), subjected to the reaction with NaETC, are as follows: CB content, 15.4 mole% from elemental analysis of chlorine and 15.3 mole% from the calculation by the Skeist method (SKEIST 1946); molecular weight by membrane osmometry, 18000. The good agreement of the CB contents by the two methods indicates that this polymer is a random copolymer characterized by the monomer reactivity ratios, i.e., $r_1 = 0.274$ and $r_2 = 1.680$ where M_1 = styrene and M_2 = CB (KOHJIYA et al. unpublished).

The time course of the reaction of the copolymer with NaETC is shown in Fig. 1.

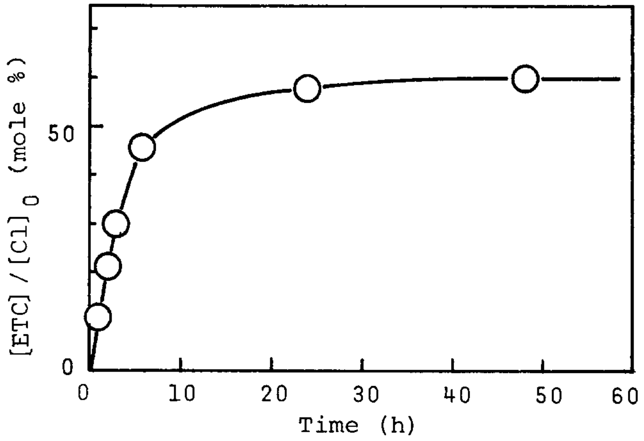
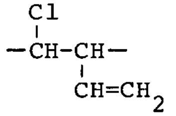
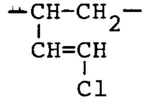


Fig. 1 Reaction Time Course of Poly(CB-co-Styrene) with NaETC in DMF at 50°C.

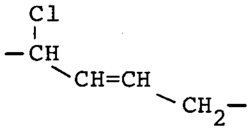
The reaction proceeded rapidly at a initial stage, but the ETC concentration was converging to a definite value after several hours. Therefore, we assumed that practically all the chlorine that was possible to be substituted by ETC group had reacted with NaETC after 24 hours. The asymptotic value is 61 percent, i.e., 61 mole% of chlorine in the copolymer were replaced by ETC group.

There are four possible microstructures in CB polymers:

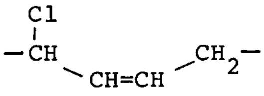
1,2

$-\overset{\text{Cl}}{\overset{|}{\text{C}}}\text{H}-\underset{\underset{\text{CH=CH}_2}{|}}{\text{C}}\text{H}-$

3,4

$-\underset{\underset{\underset{\underset{\text{Cl}}{|}}{\text{CH=CH}}}{|}}{\text{CH}}-\text{CH}_2-$

trans-1,4



cis-1,4



Among them, 1,2-microstructure was not present in CB polymers (WINSTON and WICHACHEEWA 1973, KOHJIYA et al. 1981, KOHJIYA et al. unpublished). In 1,4-microstructures, cis and trans are distinguishable only by infrared spectroscopy. Both infrared and ^1H NMR spectroscopies have shown that 1,4- and 3,4-microstructure contents in poly(CB-co-styrene)s were 60 % and 40 %, respectively (KOHJIYA et al. 1981, KOHJIYA et al. unpublished). From a chimical point of view, 1,4-microstructure carries an allylic chlorine, and 3,4 a vinylic one. Allylic chlorines are known to undergo nucleophic reactions very easily, while vinylic ones are inactive (for example, see GUTSCHE and PASTO 1975). In fact, 3-chlorobutene-1 and trans-1-chloro-2-butene (allylic) suffered the quantitative substitution by NaETC in DMF at 50°C in a few hours, but 1-chlorobutene-1 (vinylic) did not react at all under these conditions. The observed extent of the reaction (61 %) is in accord with the 1,4-microstructure content by the spectroscopies (60 %). This accordance indicates that all the chlorine on 1,4-microstructure has been substituted by ETC group, and the assayed ETC concentration is equal to that of 1,4-microstructural CB units.

Carbamation of Poly(CB-co-Bu)

Fig. 2 shows the reaction time course of poly(CB-co-Bu) with NaETC in a binary mixture of DMF and THF at 50°C. The carbamation practically ceased after 24 hours in the same manner as in Fig. 1. The CB-units contents in poly(CB-co-Bu) changes from 0 mole% (No. 1, polybutadiene) to 100 mole% (No. 8, poly(CB)). From the asymptotic [FTC] values in Fig. 2, the percent of chlorine substituted by ETC group can be evaluated. In other words, the content of 1,4-microstructural CB units in poly(CB-co-Bu) is determined by the carbamation.

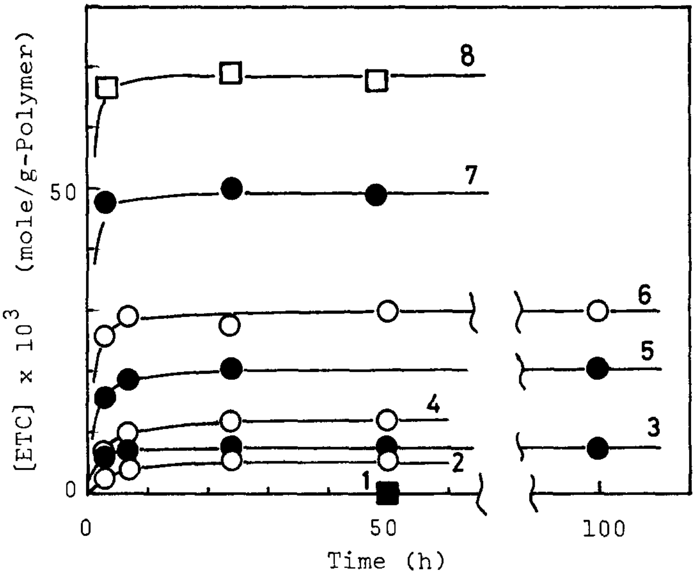


Fig. 2 Reaction Time Courses of Poly(CB-co-Bu)s with NaETC in DMF/THF(3/5) at 50°C. CB contents in mole %: 1, 0; 2, 6.7; 3, 8.5; 4, 12.7; 5, 24.7; 6, 41.7; 7, 62.9; 8, 100.

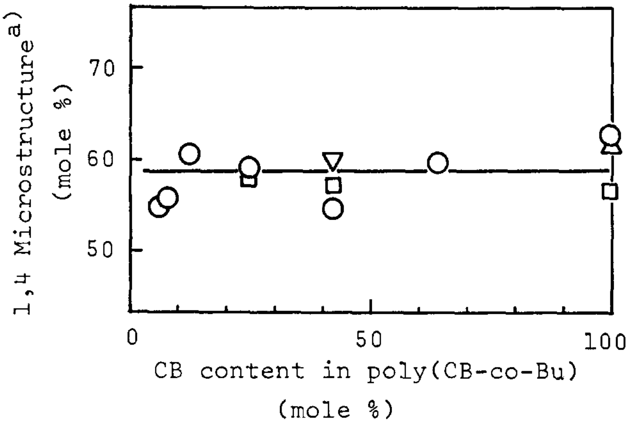


Fig. 3 1,4-Microstructure$^{a)}$ in Poly(CB-co-Bu) from Carbamation. a)1,4-Microstructure content relative to total CB units. Methods of ETC determination: ○, UV; □, elemental analysis of sulfur; △, that of nitrogen; ▽, that of chlorine.

The results are shown in Fig. 3. The percent of 1,4-microstructure in CB units seems to remain constant over the wide range of the CB contents in poly(CB-co-Bu).

TG of Poly(CB-co-Styrene) and Poly(CB-co-Bu)

TG curves of polystyrene, poly(CB-co-styrene), and ETC-poly(CB-co-styrene) are shown in Fig. 4 (Nos. 1-3).

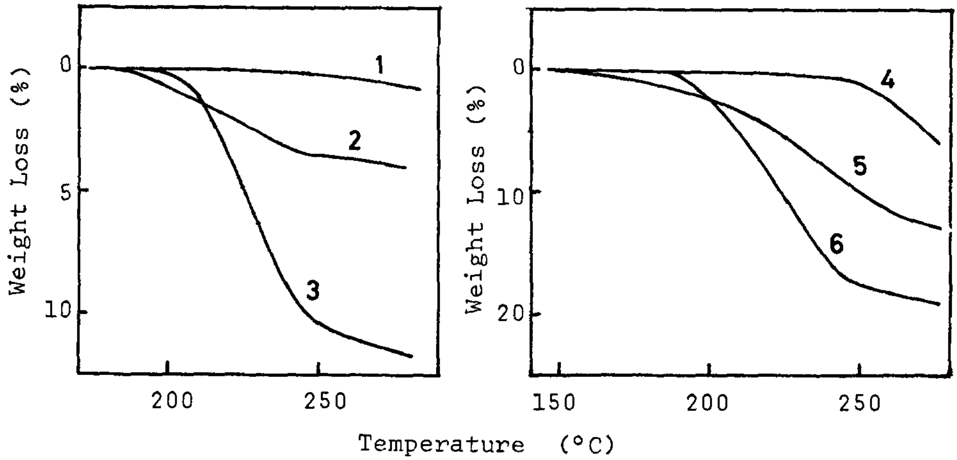


Fig. 4 TG Curves: 1, Polystyrene; 2, Poly(CB-co-styrene) (CB 15.4 mole%); 3, ETC-Poly(CB-co-styrene); 4, Polybutadiene; 5, Poly(CB-co-Bu) (CB 41.7 mole%); 6, ETC-poly(CB-co-Bu).

ETC-copolymer represents the copolymer treated with NaETC. Polystyrene did not show any weight loss until 250°C. On the other hand, poly(CB-co-styrene) (curve 2) showed 3.2-% weight loss between 180°C and 250°C. Above 250°C the slope of TG curve became smaller. This behavior can be interpreted by the hydrogen chloride elimination from CB units. If all the chlorine is eliminated as hydrogen chloride, the theoretical weight loss should be 5.53 %. Therefore, (3.2/5.53) x 100 = 58 % of the chlorine is estimated to be allylic, i.e., on 1,4-microstructural units. This value is in good agreement with that by the carbamation (61 %). TG of ETC-copolymer indicates a similar weight loss of ca. 13 % above 190°C. This weight loss is in an excellent agreement with the calculated one (13.08 %) assuming all the ETC group is eliminated as diethyldithiocarbamic acid from the ETC-copolymer.

TG curves of polybutadiene, poly(CB-co-Bu), and ETC-poly(CB-co-Bu) (Nos. 4-6) show a very similar behavior to that of poly(CB-co-styrene). However, the elimination started at lower temperature (ca. 150°C) and the point where the reaction ceased became much less clear. Weight loss between 150°C and 260°C indicated 50-% chlorine was removed as hydrogen chloride, and this value is close to the 1,4-microstructure content by carbamation (58 %). Therefore, TG on poly(CB-co-Bu) can also give a semi-quantitative information on the microstructure of CB units.

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Received October 19, 19181
Accepted November 21,1981

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