

DSC measurements on butadiene/ethene/ α -olefin terpolymers¹

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Abstract

Butadiene/ethene- and α -olefin-based terpolymers, produced with the aid of a special Ziegler–Natta catalyst, are useful as model substances to study the crystallization behaviour of polymers because they have definite side chains at defined distances on their skeletons.

There is no information in the literature concerning the syntheses of such polymers. chemical methods of analysis are not sufficient to characterize these products. It is shown that conclusions on the formation of co- and terpolymers can be drawn from the analysis of melting peaks in DSC thermograms. Thus the efficiency of the synthesis can be judged.

INTRODUCTION

Co- and terpolymerization of butadiene and α -olefins lead to the formation of interesting elastomer and thermo-plastic polymers. Furthermore, these polymers are suitable model substances for studying the crystallization behaviour with respect to the polymer structure. The synthesis of these polymers was achieved by application of a special vanadium catalyst system [1–3].

The butadiene/ethene copolymer synthesized in this way [4] was a linear polymer with a high degree of crystallinity. This corresponds to an extremely low change in specific heat capacity at the glass transition. Essential properties are given in Table 1; the typical structure and the DSC melting curve are shown in Fig. 1.

The copolymerization of butadiene/butene up to butadiene/decene resulted in completely amorphous copolymers [5]. Obviously, the side

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TABLE 1

Properties of butadiene/ethene copolymer

$$\overline{M_w} = 112\,000 \text{ g mol}^{-1}$$

$$T_g = -75^\circ\text{C}$$

$$\Delta C_p = 0.05 \text{ J g}^{-1} \text{ K}^{-1}$$

$$T_m^a = +65^\circ\text{C}$$

Heat of fusion 80 J g^{-1} Degree of crystallinity at $+25^\circ\text{C} = 51\%$

^a The maximum of the endothermic peak of the DSC heating run.

chains, shown in Fig. 2, hindered the crystallization of the main chain. The butadiene/dodecene copolymer shows a low degree of crystallinity, presumably due to the crystallization of the side chains [5].

The butadiene/ethene/propene terpolymers also show the influence of short side chains, introduced by methylene groups according to Fig. 3: with an increasing amount of propene, the degree of crystallization decreases, and thus all related properties change [5].

The aim of recent work was the synthesis of butadiene/ethene/ α -olefin (C_4 – C_{12}) terpolymers (see Fig. 4). There is no available information on the synthesis parameters. Taking into account the influence of the side chains discussed above, amorphous substances were expected. Surprisingly, DSC measurements indicated the formation of crystalline structures in these

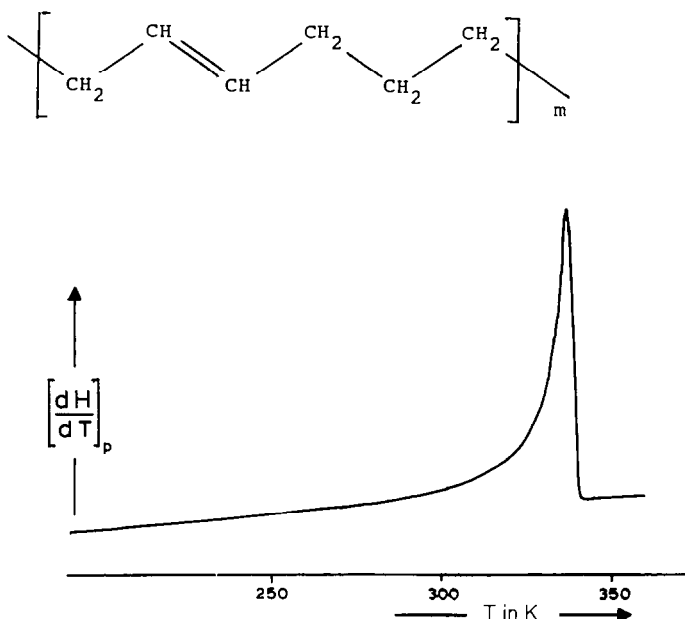


Fig. 1. Repetition unit (structural element) and DSC heating curve of butadiene/ethene copolymer.

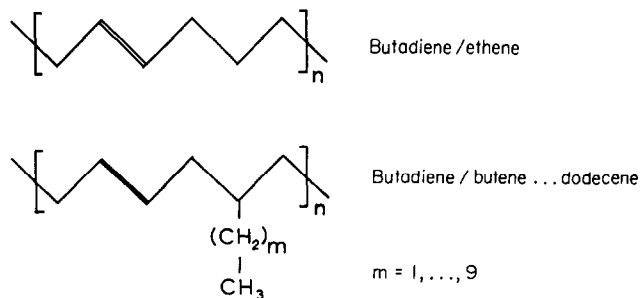
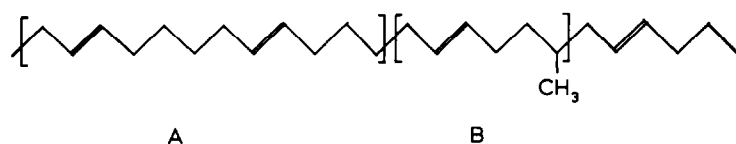
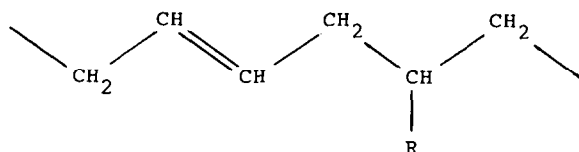
Fig. 2. Repetition units (structural elements) of butadiene/ α -olefin copolymers.

Fig. 3. Structure of butadiene/ethene/propene terpolymer.

Fig. 4. Structure to butadiene/ethene/ α -olefin terpolymers.

products, from the melting effects observed during heating. Due to structural similarities of the co- and terpolymers, obviously formed together, normal characterization methods are less powerful for the quantification of their proportions. Therefore, we tried to obtain this information from the DSC curves.

EXPERIMENTAL

The average molecular masses listed in Table 2 were determined by the common method of SEC with reference to polystyrene standards. Caloric measurements were carried out by differential scanning calorimetry using a Perkin-Elmer DSC-2. Samples of 3–5 mg were encapsulated in aluminium pans. The heating rate was 10 K min^{-1} . After the first heating scan, the samples were cooled at a rate of 10 K min^{-1} down to 170 K, the starting temperature of the second heating run. The results are summarized in Table 3.

TABLE 2

Synthesis parameters and average molecular masses of the products of terpolymerization

Sample number	Sample	Temperature of polymerization/ °C	\overline{M}_n in g mol ⁻¹	\overline{M}_w in g mol ⁻¹	Monomer ratio at the beginning	
					Bu/Ol	Et/Ol
1	Bu/Et/butene	-40	27400	52300	3.5	1.0
2	Bu/Et/pentene	-40	21800	37200	3.5	1.0
3	Bu/Et/hexene	-40	20300	39400	3.5	1.0
4	Bu/Et/octene	-40	8800	16900	3.5	1.0
5	Bu/Et/decene	-40	6600	13600	3.5	1.0
6	Bu/Et/dodecene	-40	6600	11900	3.5	1.0
7	Bu/Et/butene	-40	15100	20600	1.5	0.25
8	Bu/Et/butene	-10	18800	24200	1.5	1.0

Key: Bu, butadiene; Et, ethene; Ol, α -olefin.

TABLE 3

Results of DSC measurements of substances listed in Table 2

Sample number	Sample	Glass transition		Fusion	
		T_g in °C	ΔC_p in J g ⁻¹ K ⁻¹	Maxima of peaks in °C	Heat of fusion in J g ⁻¹
1	Bu/Et/butene	-79	0.07	49; 65	59
2	Bu/Et/pentene	-78	0.09	47; 65	70
3	Bu/Et/hexene	-77	0.05	49; 65	70
4	Bu/Et/octene	-79	0.10	49; 65	70
5	Bu/Et/decene	-79	0.13	45; 65	70
6	Bu/Et/dodecene	-76	0.13	45; 65	67
7	Bu/Et/butene	-82	0.22	22; 63	42
8	Bu/Et/butene	-78	0.07	62	69

RESULTS

The DSC curves (Figs. 5–7) for all substances show more or less large melting effects with different structures. The different degrees of crystallinity are also reflected in different heats of fusion and c_p changes at glass transition, respectively. However, clearly defined maxima of melting peaks at about 65°C could be observed in all substances. In comparison with the butadiene/ethene copolymer melting behaviour (Table 1, Fig. 1), this

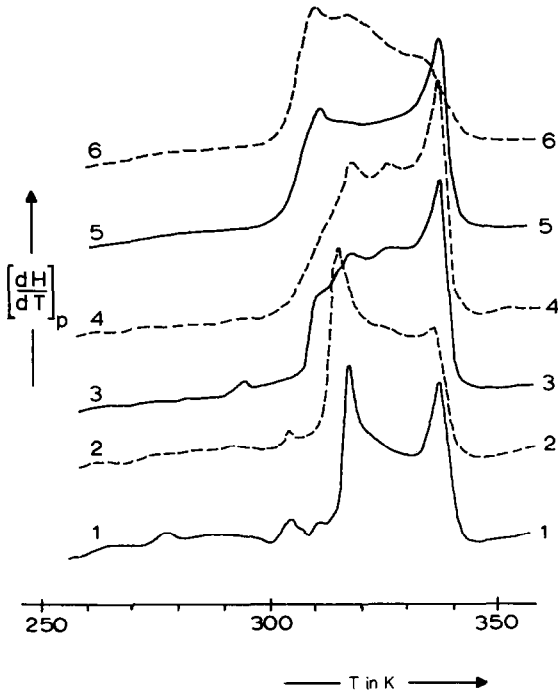


Fig. 5. DSC curves (first heating) of samples 1–6 of Tables 2 and 3.

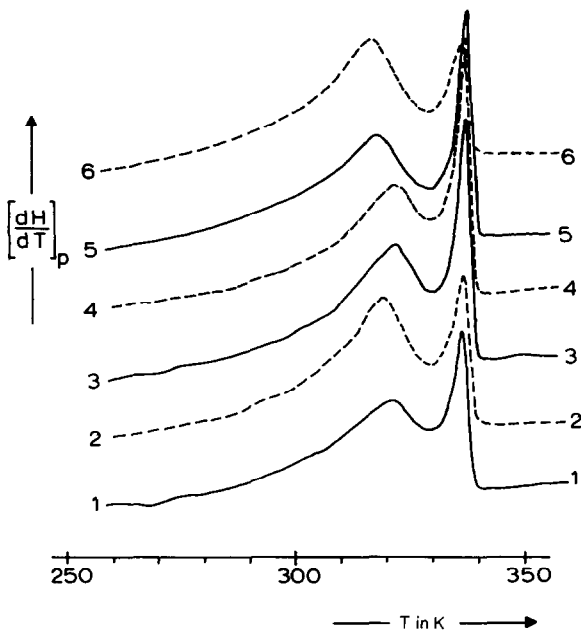


Fig. 6. DSC curves (second run after slow cooling) of samples 1–6 of Tables 2 and 3.

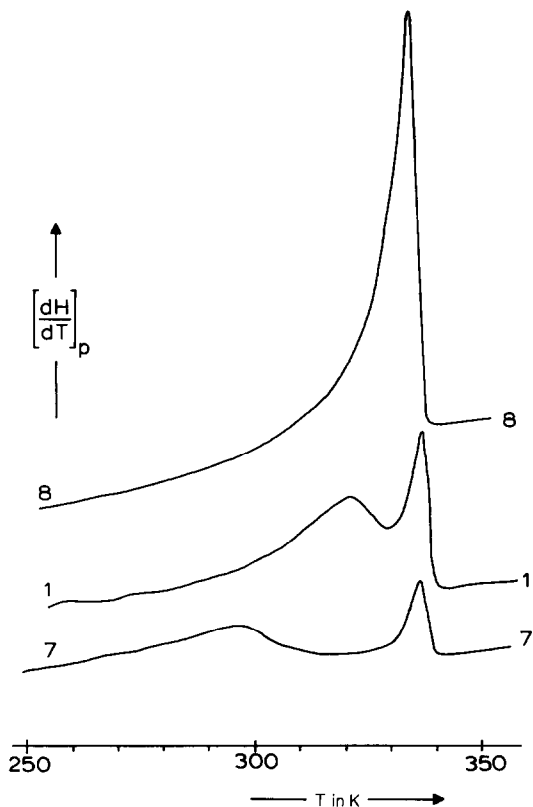


Fig. 7. DSC curves of butadiene/ethene/butene terpolymers (samples 1, 7, 8) with different synthesis parameters (see Table 2).

indicates similar structures in the samples under investigation. By changing the monomer ratio at the beginning to higher olefine amounts (sample 7), the temperatures of melting peaks and the magnitudes of the heats of fusion decrease as the degrees of crystallization decrease. If, however, the temperature of polymerization is increased (sample 8), the DSC curve is almost identical to the melting peak of the butadiene/ethene copolymer alone. The butene content in this sample was 1.3 mol.%, compared to 6 mol.% in sample 7, as measured by NMR spectroscopy.

From the literature, for example, refs. 6 and 7, the fusion temperatures T of n -alkanes are well known. Plotting the reciprocal of the number of carbon atoms $1/n$ against $1/T$ (including the melting temperature of chain-extended polyethylene [8]) gives a linear relation, as shown in Fig. 8. However, the corresponding graph for α -olefins published in ref. 6 is curved. This is understandable because, with increasing number of carbon atoms, the influence of the double bond is decreased and the substance will become more and more paraffin-like. Thus, the curve approaches asymptotically that of the n -alkanes. The extent to which the structural

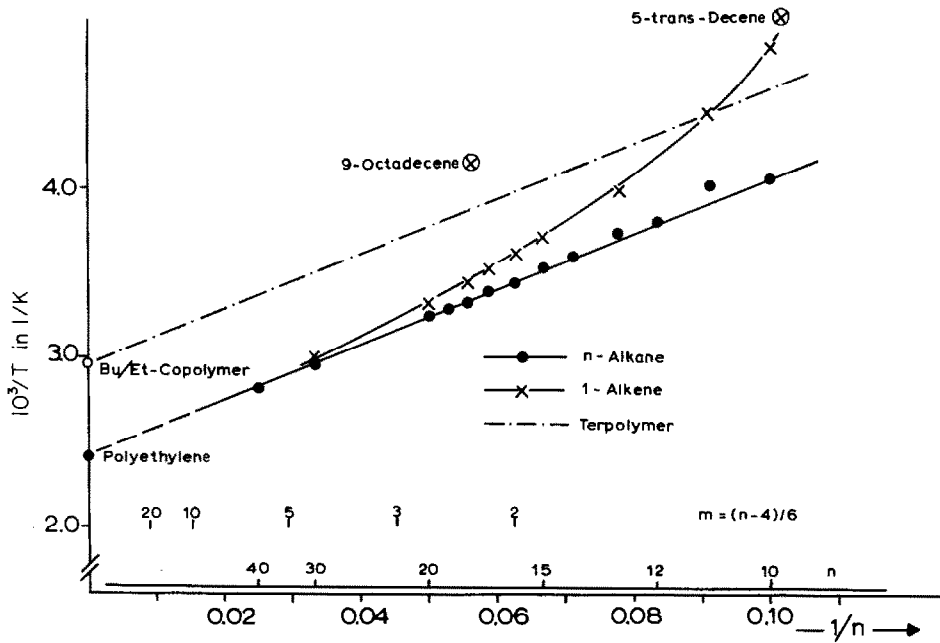


Fig. 8. Connection between temperature of fusion and number of C atoms of the chain in the polymer crystals.

effects that depend on the position of the double bond contribute is shown by the data of 9-octadecene and 5-decene (trans) [9]. Analogous to the *n*-alkanes for which the melting point of chain-extended polyethylene is used as the end point of the curve, it should be possible to use the melting point of the above-mentioned butadiene/ethene copolymer as the end point of a corresponding curve for such homologues. A curve which connects the fusion temperature with the number of carbon atoms within the crystallizing part results. This line may obviously be obtained by a parallel displacement of that for *n*-alkanes but through the new end point. This yields the relation

$$1/T_p = 0.002957 + 0.01628/n \tag{1}$$

where T_p is the peak temperature and n the number of carbon atoms. According to Fig. 9, such a polymer chain is to be comprehended as an m -times repetition of the copolymer and interpolymer unit. Thus, for

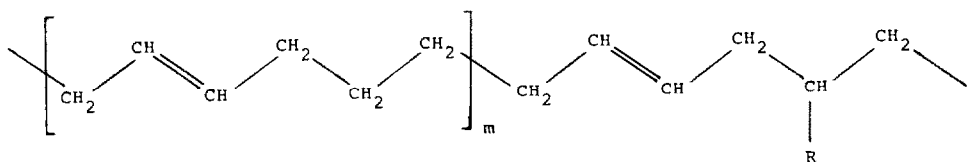


Fig. 9. Proposed structure for the synthesized polymers.

TABLE 4

Connection between number of C atoms n and the temperature of fusion from eqns. (1) and (2)

n	m	T_p/K	$T_p/^\circ\text{C}$
10	1	218	-55
16	2	252	-22
22	3	270	-3
28	4	283	+9
34	5	291	18
40	6	297	24
76	12	315	42
88	14	318	45
100	16	320	49
112	18	322	55
184	30	328	

butadiene/ethene/ α -olefin co- and terpolymers, n is given by

$$n = 6m + 4 \quad (2)$$

and the relation between the unknown chain length of the crystalline regions and the melting point is given by eqn (1). Examples of this connection are given in Table 4.

The derived function does not claim general validity, but it allows the interpretation of rapidly gained DSC curves and yields a rapid evaluation of the synthesis results. With this method, it is possible to explain the peaks with maxima at 65°C and some other peaks at lower temperatures as an effect of the simultaneous synthesis of the butadiene/ethene copolymer and different terpolymers. Furthermore, the variation of the terpolymer structures with different synthesis parameters can be explained. The second heating runs of samples 1, 7 and 8 shows in Fig. 7 are a good example of this influence: the fraction of butadiene/ethene copolymer and the fusion temperature of the terpolymer are reduced by decreasing the temperature of polymerization and by increasing the α -olefin portion in the monomer ratio. Changing these parameters in the opposite direction results in a departure from the original aim of the synthesis.

The different appearance of the curves from the first and second heating run can be explained as follows: during the first heating, the crystallites that melt had been formed by a precipitation process, and in the second heating, the melted crystals had been formed from a melt; in the second heating scan, the thermal resistance between sample and sensor is notably decreased owing to improved contact between sample and pan.

Chemical reactions during the melting can be excluded. From a methodical point of view the second heating scans are more important and

provide more information. Peak maxima below 65°C do not reflect a discrete chain length or an exact number of carbon atoms, but a statistical average of different chain lengths or lamellae thicknesses.

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