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Characterization of ethylene homo- and copolymers*

VI. Determination of chemical composition of (norbornene ethylene) copolymers

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Summary

For (norbornene ethylene) copolymers with a preferably alternating structure two methods for the determination of chemical composition were tested: the differential refractometry (DR) and the differential scanning calorimetry (DSC). It was found, that the refractive index increments measured by DR in 1,2,4-trichlorobenzene can be calculated by adding the refractive index increments of the homopolymers with regard to the composition of the copolymers. This was proved by comparing with results obtained by 1H-NMR-measurements. The temperatures of the glass transition determined by DSC yield a straight line correlation to the chemical composition. Errors of both methods due to the influence of molecular masses are negligible and of significance only in the range of low molecular masses.

Introduction

(Norbornene ethylene) copolymers (NEC) can be synthesized by polymerization of the monomers using a modified ZIEGLER catalyst [1]. In this case the norbornene is polymerized as a vinyl compound and its ring system is conserved [2,3]. For the molecular characterization of such copolymers the size exclusion chromatography has proved to be suitable [4]. The determination of the chemical composition is possible by NMR-measurments [2,3]. For copolymers precipitated during the polymerization an approximately equimolecular composition and a preferably alternating structure could be found. On the other hand samples polymerized in solution showed also deviations from the alternating arrangement and, hence, from the equimolecular composition. Consequently, the determination of the chemical composition will always be necessary for a comprehensive characterization of such products.

Therefore, two further practicable methods for the determination of the chemical composition of NEC are proposed: the differential refractometry and the differential scanning calorimetry.

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Differential refractometry (DR)

The method is based on the significant difference of the refractive index increments dn/dc of polyethylene and polynorbornene dissolved in a suitable solvent. For a mixture of these homopolymers the refractive index increment of the solution is calculated by equation (1).

$$dn/dc = x\,[dn/dc]_E + (1-x)\,[dn/dc]_N \qquad (1)$$

$[dn/dc]_E$, $[dn/dc]_N$ = refractive index increments of polyethylene and polynorbornene
x = mass portion of polyethylene in the mixture

The validitiy of this relation was confirmed also for several other copolymers [5] without any reference as to the distribution of the sequences of the monomer units. The additivity of refractive index increments according to equation (1) should be valid, in all probability, also for block copolymers. For random and alternating copolymers it cannot always be expected, especially if interactions take place between the structural elements of the different monomer units. Since relatively indifferent monomer units are present in NEC, the validity of equation (1) is very likely. This makes it possible to determine quantitatively the chemical composition.

If the conditions of measurement (temperature, solvent, concentration of the solution) are held constant and the differential quotients are substituted by difference quotients, equation (1) turns into (2).

$$\Delta n = x \cdot \Delta n_E + (1-x) \cdot \Delta n_N \qquad (2)$$

Hence it follows for the mass portion of ethylen in the copolymer:

$$x = \frac{\Delta n - \Delta n_N}{\Delta n_E - \Delta n_N} \qquad (3)$$

Differential scanning calorimetry (DSC)

As a result of the preferably alternating structure NEC's are amorphous and show a glass transition in the DSC-diagram. The temperature interval is about 10...20 °C, and the change of the specific heat is relatively insignificant due to the stiffness of the norbornene units. The perceptibility of glass transition in the DSC-curve can be improved by thermal pretreatment of the sample prior to measurement. As a result of the slow cooling of the sample from the melt to a temperature below glass transition a very extensive enthalpic and volume relaxation takes place, and by the quick heating of the sample during measurement the temperature range of the glass transition becomes narrower and the change in heat capacity higher.

The glass transition temperature (T_g) is taken as the midpoint in the thermogramm as measured from the extensions of the pre- and post-transition baselines; that is, when the change in heat capacity is half the total value of the change through the transition. This value can be determined experimentally most exactly and shows only an insignificant dependence on the conditions of measurement.

The glass transition temperature is strongly influenced by structural and molecular factors. In pfropf and block copolymers two-phase systems are present, which involve a separate glass transition for each phase. In random and alternating copolymers only a single phase exists and hence only one T_g, which, therefore, mostly is located between the values of the corresponding homopolymers if no interactions take place between the components of the copolymers. In the case of NEC such effects hardly can be anticipated, so that for the position of the glass transition temperature in dependence on the copolymere composition a relation according to [6] is expected:

$$T_g = \sum n_i \, T_{g,i} \qquad (4)$$

n_i = molar fraction of rotatable bonds of the component i

$T_{g,i}$ = T_g of the homopolymer componente i

After proper calibration the determination of the composition is possible, in view of the fact that the glass transition temperature of the homopolymers are extremly different, as in NEC. One should not neglect the influence of the molecular masses and of oligomers possibly present or of low-molecular impurities, which are compatible with NEC and influence the T_g showing something like a plasticizer effect. Previous experience [7] has shown that, as a result of the high mobility of the chain ends, a straight line correlation between T_g and the reciprocal molecular masses can be found. Therefore, it is necessary to examine quantitatively or estimate the size of these effects.

Experimental

The experimental DR-measurements were performed at 135 °C in 1,2,4-trichlorobenzene at a concentration of 0.25 mass-%. 1,2,4-trichlorobenzene yielded for a equimolecular NEC a refractive index increment of about 0 cm^3/g. Therefore, deviations from this composition are at once clearly perceptible. Δn was measured with the differential refractometer of a WATERS ANA-PREP Gel permeation chromatograph as the difference to the pure solvent. Moreever, the whole chromatographic system of the analytical part of the chromatograph was used. The solution of the sample (2 cm^3) was injected into the continuously flowing solvent and led through at least one styragel column to the detector. By use of a proper column set [4] the simultaneous separation according to the molecular masses is possible and, hence, a prediction about the dependence of chemical composition on molecular masses. Δn can be obtained by integration of the chromatographic peak as a relative value. The calibration and determination of Δn_N and Δn_E was performed with homopolymers produced under similar polymerization conditions. The mass portions calculated according to equation (3) allow to calculate the molar composition in the usual way.

The DSC was performed by a DSC 1B of Perkin-Elmer. The sample quantity was 5...10 mg. At first the samples were melted above the glass transition temperature and slowly cooled down (0.2 °C/min). The T_g was measured at a heat rate of 16 °C/min. The melting of the sample prior to measurement not only served for a better perceptibility of the glass transition temperature, as described above, but also for the removal of the volatile ingredients of low molecular masses. The content of such ingredients can be determined by thermogravimetry. At temperatures above the glass transition temperature (150... 200 °C) the ingredients quantitatively escape and lead to a corresponding mass loss. Consequently, the melting of the sample prior to T_g-measurement excludes to a high degree incorrectness of the T_g as a result of possible ingredients of this kind.

The examined samples were synthesized at a modified Ziegler catalyst [1] varying the monomere portion within a very broad range. Preparative quantities of fractions of different molecular masses were gained by fractionation of the sample 7 according to the method of Desreux et al. [8] and Francis et al. [9] using mixtures of tetrahydronaphthaline and 2-ethoxyethanol with continuously altering composition at a temperature of 130 °C. The determination of molecular masses was performed according to [4].

Results

Table 1 summarizes the copolymere compositions (contents of ethylene) determined by DR for a series of samples and the measured glass transition temperatures T_g. A steep decrease of T_g with increasing contents of ethylene can be stated. Fig. 1 shows a graphical representation of these results. The mentioned dependence can be rather well described by a straight line. Considering samples 1 through 11 regression analysis led to the following correlation:

$$x_E = 79.72 - 0.2208\, T_g \qquad (x_E \text{ in mol-\%}) \qquad (4)$$

correlation coefficient: 0.990

Table 1 also contains the ethylene contents calculated from T_g according to equation (4) and permits to identify the ex-

Table 1: Results of the DR- and DSC-measurements

Sample	Ethylene content [mass-%]	[mol-%]	T_g(DSC) [°C]	Ethylene content (DSC) according to eq. (4) [mol-%]
1	18.1	42.6	167.8	42.7
2	19.0	44.1	159.8	44.4
3	19.5	44.8	160.7	44.2
4	21.4	47.8	142.9	48.2
5	22.1	48.8	142.7	48.2
6	22.6	49.5	134.4	50.0
7	24.0	51.5	126.0	51.9
8	24.1	51.6	127.3	51.6
9	25.4	53.3	122.9	52.6
10	26.7	55.0	106.5	56.2
11	29.5	58.4	101.3	57.4
12*	20.5	46.4	153.6	45.8
13*	21.6	48.0	146.4	47.4
14*	32.7	62.0	112.9	54.8

* 1H-NMR-results [3]:
sample 12: 46 mol-%
sample 13: 48 mol-%
sample 14: 55 mol-% (contains 7.5 mol-% as polyethylene)

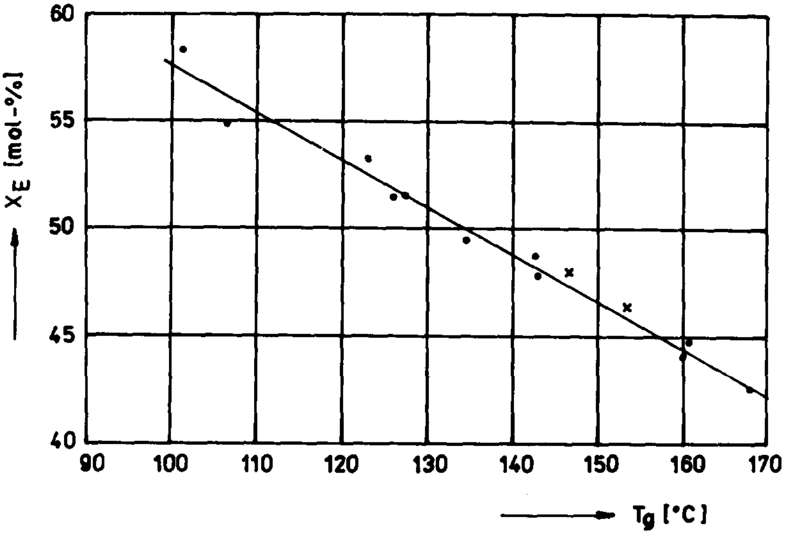

Fig. 1: Correlation between ethylene content x_E (DR) and glass transition temperature T_g (× samples 12 and 13)

perimental, statistic errors of both methods. For the sample 12 through 14 the copolymer composition was additionally determined by 1H-NMR [3], which allows an estimate of the systematic error of the methods.

Table 2 represents the results obtained for the fractions of sample 7. Fig. 2 showes the graph of T_g in dependence on the reciprocal molecular masses. In spite of scattered measuring points a straight correlation in the range of low molecular masses is perceptible, whereas in the range higher than $2 \cdot 10^4$ g/mol the molecular mass scarcely influences the T_g. The scattering of the measuring points is mainly caused by experimental errors, but probably also by small differences in the chemical composition.

Discussion

From the comparison of the copolymer composition obtained by DR and from T_g (Table 1) a medium sqare deviation of ±0.7 mol-% ethylene (max. deviation: 1.2 mol-%) was calculated. Also the statistical errors of both methods should be about the same. The larger deviation for sample 14 can be explained from the content of polyethylene, obtainable from the DSC-curve. Polyethylene has a separate melt peak of 133 ± 1 °C. With regard to the melt enthalpy of a polyethylene obtained and measured under the same experimental conditions (ΔH = 141.8 J/g) the content can be calculated from the peak area provided the melt peak is completely separated from the T_g-step. The polyethylene content also can be obtained from DR, if a proper column set is used which separates the NEC from the polyethylene. The separation is possible, as the polyethylene mostly is very high-molecular.

The good agreement of the ethylene contents obtained by NMR for some samples with those found by DR or DSC proves, that the assumed additivity of the refractive index increments is correct. Therefore, the systematic error of the introduced methods should be not greater than the statistical one.

The DSC measurements for the fractions show that the dependence of the T_g on molecular masses is essentially smaller than the dependence on chemical composition. The technical relevant NEC's have medium molecular masses higher than $2 \cdot 10^4$ g/mol and only small portions of lower molecular masses [4]. Therefore, the possible determination errors of the chemical composition by T_g measurement are insignificant and negligible. The same is also true for errors, which can be caused by the dependence of the refractive index increments on the molecular masses. Determinations of the refractive index increments in dependence on the molecular masses were published mainly for polystyrene [10,11,12] but also for polyisoprene [12], polydimethylsiloxane [13], and polyethylene [11]. In most cases only below 10^4 g/mol the authors found a significant influence of the molecular masses in dependence on the used solvent. Above $10^4 \ldots 2 \cdot 10^4$ g/mol only a small or no effect was observed.

Table 2: Results of measurements for the fractions of sample 7

Fr.-N.	$\bar{M}_w \cdot 10^{-3}$ [g/mol]	$10^6/\bar{M}_w$ [mol/g]	T_g(DSC) [°C]	content of ethylene	
				from T_g [mol-%]	from DR [mol-%]
1	8.9	112.4	114.1	54.5	49.4
2	17.3	57.9	125.3	52.1	51.0
3	19.5	51.3	123.1	52.5	52.9
4	27.3	36.6	126.0	51.9	50.2
5	29.3	34.1	130.6	50.9	51.5
6	30.4	32.9	125.9	51.9	51.5
7	34.0	29.4	131.0	50.8	
8	37.2	26.9	129.8	51.1	
9	38.8	25.8	130.8	50.8	
10	43.7	22.9	130.6	50.9	
11	49.0	20.4	124.0	52.3	
12	55.0	18.2	129.6	51.1	

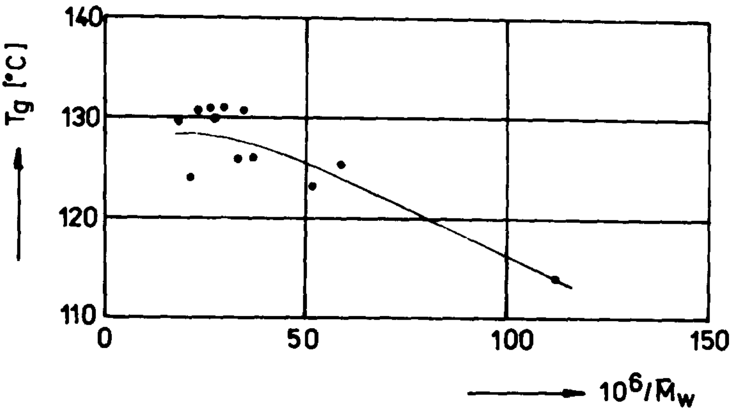

Fig. 2: Glass transition temperature in dependence on the reciprocal molecular masses for the fractions of sample 7

The results according to table 1 confirm the preferably alternating structure of the copolymers. Notwithstanding the great variation of the monomere portions used for the synthesis, the chemical composition deviates only a little from the equimolecular composition (ethylene contents of 43...55 mol-%). This indicates low copolymerization parameters, which were found at $r_N = 0.0035$ and $r_E = 0.30$ [3,14]. The calculated product $r_N \cdot r_E = 0.001 \sim 0$ allows to expect a preferably alternating structure.

The results according to table 2 show a nearly uniform chemical structure in dependence on the molecular masses. The ethylene contents obtained in the range of 51.6...53.1 mol-% are attributable to the experimental error. The correctness of the result measured for the low-molecular fraction 1 is questionable as the resulting values of both methods are significantly different. There is reason to suppose the molecular mass effect influences both methods.

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