COMPREHENSIVE THERMAL ANALYSIS OF RANDOM COPOLYMERS OF ETHYLENE AND 1-OLEFINS

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Random copolymers of ethylene and propylene, butene-1 and hexene-1 were characterised by measurements of heat capacity in the temperature interval 140–480 K and specific volume of the melt in the temperature interval 330–490 K and in the range of pressures 27.8–100 MPa. Analysis of the composition dependences, of the degree of crystallinity, melting and glass transition temperatures, as well as of thermodynamic and thermophysical properties of the melt led to the conclusion about the microblock structure of macromolecules of all series at molar ethylene content $F_1 > 0.8$. In this range of compositions the properties of copolymers in the melt seem to be independent of the chemical nature of a comonomer, contrary to the solid state where at identical molar compositions, the degree of crystallinity diminishes and the melting temperature decreases, as the molecular structure of the comonomer becomes more complex. This effect becomes weaker as F_1 decreases, so that in the composition range $F_1 < 0.8$ the properties of copolymers of all series are additive.

Keywords: copolymers of ethylene and 1-olefins, thermal analysis

Introduction

Classical theory predicts [1] that intramolecular 'dilution' of a polymer 1 with foreign monomeric units 2 lowers the thermodynamic stability of a crystalline phase of the former as explicitly stated by the following equation:

$$\frac{1}{T_m} - \frac{1}{T_m^o} = -\left(\frac{R}{\Delta H_m^o}\right)\ln p,$$

(1)

where T_m^o and ΔH_m^o are the melting point and melting enthalpy of the pure crystalline phase, 1, p is the probability that an arbitrary chosen monomeric unit of the crystallizable component 1 in the copolymer chain is bonded to an identical monomeric unit 1 (in the case of random copolymers this probability may be identified as the mole fraction of component 1, F_1), T_m is the melting point of the

crystalline phase of a copolymer with composition F_1. It follows from Eq. (1) that the melting point depression of a copolymer depends solely on the molar fraction $(1- F_1)$ of comonomer 2 but not on the chemical nature of the latter. This conclusion found experimental support in the studies of random copolymers of ethylene (component 1) and 1 olefins (component 2) at high ethylene contents ($F_1 > 0.97$) [1– 3], while the melting point depression was found to increase at lower values of F_1, with the length of the side alkyl radical [4, 5]. The origin of such behaviour still remains somewhat obscure, however, there are reasons to believe that it has something to deal with the possibility of sufficiently long alkyl radicals to exhibit their own thermal mobility in the melt phase [6], thus hindering the crystallization. It seemed worthwhile therefore to study the influence of the chemical nature of 1-olefins on other thermophysical properties of their random copolymers with ethylene.

Experimental

Random copolymers of ethylene and propylene (series CEP), 1-butene (series CEB) and 1-hexene (series CEH) were obtained by ionic coordination copolymerization on complex metal organic catalysts [7]. The mole fraction of ethylene in the copolymer chain, F_1, was determined by IR spectroscopy (maximum error below 2.5%) according to recommended procedures [2, 7, 8]; fractions of like (f_{11}, f_{22}) and unlike ($f_{12} = f_{21}$) dyads in the chain were calculated by the following formulas [7]:

$$f_{11} = r_1\frac{F}{K}; \quad f_{12} = \frac{1}{K}; \quad f_{22} = \frac{r_2}{FK};$$

where $K = r_1 F + 2 + r_2/F$; F is the molar ratio of monomers 1 and 2 in the starting reaction mixture, r_1 and r_2 are reactivities of ethylene and 1-olefin, respectively (in calculations we used $r_1 = 5.6$ and $r_2 = 0.14$ for CEP [7], $r_1 = 12.5$ and $r_2 = 0.03$ for CEB [4]. Lacking the needed experimental data for CEH, we used $r_1 = 16$ and $r_2 = 0.05$ as for copolymers of ethylene and 1-octene [4]).

The heat capacity of 'annealed' (i.e., slowly cooled from the melt) and 'quenched' (produced by immersion of the molten polymer in liquid nitrogen) samples was measured (relative error about 3%) in the temperature interval 140–480 K with the aid of a differential calorimeter with diathermal cells [9] at a heating rate of 2 deg/min.

Equilibrium values of the melt specific volume V in the temperature interval 330–490 K and in the pressure range 27.8–100 MPA were measured using a thermopiezometer [10] (maximum uncertainty $5 \cdot 10^{-7}$ m^3/kg), the specific volume at normal pressure, V_o, was estimated with the aid of the Tait equation,

$$1 - \frac{v}{v_0} = 0.08941n \left(1 + \frac{P}{B} \right),$$

as that assuring minimum variation of parameter B at each temperature in the whole experimental pressure range.

An instantaneous (i.e., quasiadiabatic) pressure jump, ΔP = 9.7 MPA, in the compression chamber of thermopiezometer is accompanied by a sudden jump of the melt temperature from T_0 up to T_{max} and subsequent slow temperature relaxation down to the starting temperature T_0 due to equilibration of temperature fields within the specimen by thermal diffusivity mechanism. The thermal diffusivity, a, was determined with a mean error of about 2% as the slope of the straight line on the plot of the function $\ln \tau$ *vs.* time t (here $\tau = (T - T_0)/(T_{max} - T_0)$ is the reduced temperature, and T is the transient temperature of the sample in the course of relaxation.

Results and discussion

Thermal transitions

The heat capacity of all annealed samples studied, passes through relatively small jumps ΔC_p at the glass transition temperature T_g of the amorphous phase and endothermic heat effects with peaks corresponding to the melting point of the crystalline phase T_m. Quenching results in the increase of ΔC_p and in the appearance in several cases of exothermic peaks of 'cold crystallization' some 30 –40 K above T_g.

As can be seen from the data collected in Table 1, both the melting temperature of the crystalline phase T_m and the degree of crystallinity expressed as the experimental heat of melting, ΔH_m^*, for annealed samples of all series regularly decrease with F_1, this effect manifesting itself more strongly, in samples of the series CEB and CEH as compared to those for series CEP. According to theory [1] the dependence of the equilibrium degree of crystallinity X of a random copolymer on its composition is expressed as:

$$X = \frac{F_1}{p} (1-p)^2 p^{\zeta^*} \left\{ p (1-p)^{-2} - e^{-\Theta} (1 - e^{-\Theta})^{-2} + \zeta^* [(1-p)^{-1} - (1 - e^{-\Theta})^{-1}] \right\}, \quad (2)$$

where
$$\zeta^* = - \frac{\ln \left(\frac{DF_1}{p} \right) + 2\ln \left(\frac{1-p}{1 - e^{-\Theta}} \right)}{\Theta + \ln p}$$

is the critical number of monomeric units in a continuous sequence of component 1 which is necessary to crystallization; $\theta = (H_m^o / R) (1/T - 1/T_m^o)$ is the reduced

Table 1

Polymer	F_1	T_m / K	ΔH_m / kJ kg^{-1}	T_g / K	ΔC_g / kJ kg^{-1} K^{-1}
Polyethylene	1.00	407	230	—	—
CEP–02	0.98	397	182	—	—
CEP–04	0.96	396	153	—	—
CEP–06	0.94	389	152	252	0.15
CEP–10	0.90	387	97	243	0.16
CEP–22	0.78	387	51	228	0.36
CEP–43	0.57	—	—	220	0.44
CEP–63	0.37	—	—	229	0.43
CEP–68	0.32	—	—	233	0.44
CEP–94	0.06	418	50	250	0.36
Polypropylene	0.00	433	80	258	—
CEB–012	0.988	395	160	—	—
CEB–025	0.975	393	143	—	—
CEB–06	0.94	393	125	245	0.20
CEB–15	0.85	378	8	237	0.38
CEB–27	0.73	—	—	224	0.47
CEB–45	0.55	—	—	233	0.49
CEB–58	0.42	—	—	229	0.47
CEB–80	0.20	384	87	234	0.40
CEB–89	0.11	385	88	236	0.38
Polybutene–1	0.00	393	90	240	0.40
CEH–003	0.997	403	186	—	—
CEH–015	0.985	398	142	—	—
CEH–02	0.98	393	150	—	—
CEH–03	0.97	393	127	248	0.13
CEH–04	0.96	392	92	243	0.16
CEH–055	0.945	391	98	236	0.20
CEH–068	0.932	389	80	231	0.20
CEH–078	0.921	391	62	238	0.30
CEH–95	0.05	—	—	218	0.32
Polyhexene–1	0.00	—	—	228	0.29

degree of undercooling, $D = \exp(-2\,\sigma_e\,/RT)$ is the contribution of interfacial energy, σ_e, at the boundary, melt-crystal end face, to the thermodynamic barrier to crystallization.

Theoretical dependences of ΔH_m^* on F_1 calculated with the aid of Eq. (2) are shown as double-logarithmic plots in Fig. 1 (in the calculations we employed F_1 $= p$, $T_m^o = 406$ K, $\Delta H_m^o = 230$ kJ/kg and $T = 300$ K at variable $\ln D$). For samples of series CEP the approximately linear change of $\log H_m^*$ with $\log F_1$ cannot be described by Eq. (2) in the whole composition range, although one observes a reasonable agreement between theory and experiment in the range $F_1 > 0.9\,0$ at $\ln D = -5$ and $\zeta = 16$–18, and in the range $F_1 < 0.90$ at $\ln D = -1$ and $\zeta^* = 10$–13. The lower degrees of crystallinity for samples of series CEB and CEH can be accounted for by Eq. (2) at $\ln D = -15$ and $\zeta = 30$–33.
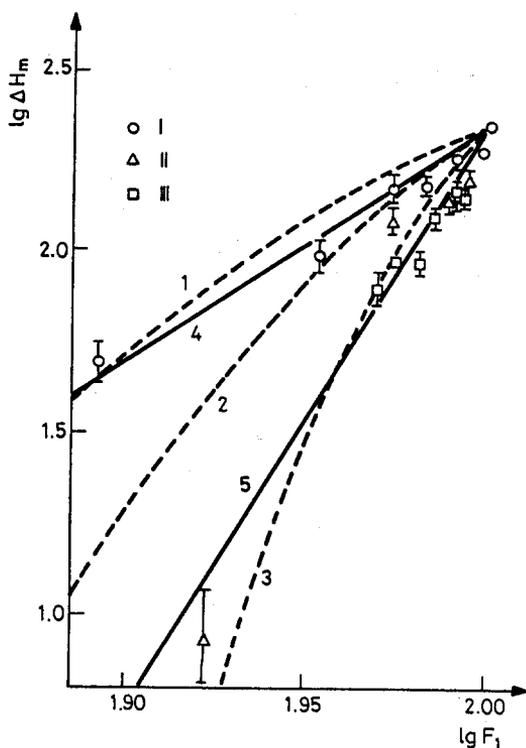

Fig. 1 Composition dependence of the melting heat of the crystalline phase of copolymers of series CEP (I), CEB (II) and CEH (III). Curves 1, 2, 3 were constructed using Eq. (2), and straight lines 4, 5 — using Eq. (3) and data from the text

It follows from the above analysis that the experimentally observed trend of a decrease in the degree of copolymer crystallinity at the same molar composition

as one goes from series CEP to series CEB and CEH may be interpreted in terms of the equilibrium theory [1] only at the expense of an increase of the thermodynamic barrier to the crystallization D. However, the increase of parameter σ_e by several orders of magnitude which is needed to account for this latter effect has, obviously, no physical meaning. Moreover, as already stated, Eq. (2) cannot reproduce the observed linear dependence of $\log H_m^*$ on $\log F_1$ which can be described by the following empirical formula:

$$\log H_m^* \text{ (in kJ/kg)} = A + B \log F_1 \qquad (3)$$

where $A = -10.8 \pm 2.2$, $B = 6.6 \pm 0.9$ for series CEP, and $A = -30.4 \pm 3.4$, $B = 16.4 \pm 1.3$ for series CEB and CEH (Fig. 1). It is remarkable that the values of the empirical parameter B which is believed to be a measure of the critical length of a continuous sequence of monomeric units of a crystallizable component of the copolymer chain [11], are about one half of the calculated values of parameter ζ^* in Eq. (2), both parameters tending to increase as one passes from series CEP to series CEB and CEH.

As can be seen from Table 1, the depression of the melting point T_m is diminishing, with decreasing F_1 for the samples of all series. According to our preliminary estimates, such behaviour cannot be explained by Eq. (1) since this would require variation of both p and ΔH_m^* with composition. It can be supposed that the observed discrepancy is caused by the dependence of T_m not only on F_1 but on the crystal height l as predicted by the following relationship [1]:

$$T_m = T_m^o (1 - 2\sigma_e / \Delta H_m^o \, l, \qquad (4)$$

where in this case the values of T_m^o and ΔH_m^o refer to the crystalline phase of homopolymer 1 as l does to infinity. Assuming that the 'bulk' degree of crystallization of a copolymer X is the same as the 'linear' crystallinity, $X = l/(l + n \, l_o)$ [12], substituting $l = X n \, l_o / (1 - X)$ and $X = 10^A F_1^B$ from Eqs (3) into (4), we obtain after arrangements:

$$T_m = T_m^o - \frac{C}{n}\left(\frac{1}{10^A} F_1^B - 1\right) \qquad (5)$$

where n is the number of chain single bonds of a length of $l_o = 1.27 \cdot 10^{-10}$ m which were squeezed out into intercrystalline space, $C = 2\sigma_e \, T_m^o / \Delta H_m^o \, l_o$.

Theoretical dependences of T_m on the copolymer composition calculated by Eq. (5) with $\sigma_e = 80 \cdot 10^3$ J/m^2, $T_m^o = 406$ K, $\Delta H_m^o = 28$ kJ /m^3 [12, 13] and values of parameters A and B from Eq. (3) cited above for different copolymer series and variable values of parameter n are shown in Fig. 2. As was already observed in the discussion of similar data within the framework of Eq. (1), the dependence of

experimental values of T_m on F_1 may be described by Eq. (5) only by assuming that parameter n regularly increases from 50 to 400 as F_1 decreases.
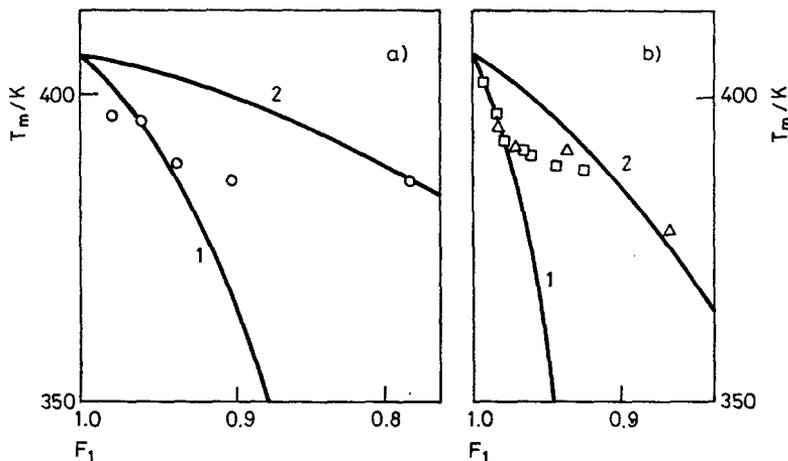

Fig. 2 Composition dependence of the melting temperatures of the crystalline phase of copolymers of series CEP (a), CEB and CEH (b). Curves 1 and 2 were constructed using Eq. (5) and data from the text

Glass transition temperatures T_g and corresponding heat capacity jumps ΔC_p of the amorphous phase of quenched samples of series CEB are plotted vs. composition in Fig. 3. Similar plots were constructed for the other series. Provided that crystallinity does not interfere, any thermodynamic property of the amorphous phase of a copolymer, to the first approximation, must obey the following obvious additive relationship [14]:

$$Z = Z_{11}f_{11} + 2Z_{12}f_{12} + Z_{22}f_{22} \qquad (6)$$

where Z_{11}, Z_{22} and Z_{12} are the 'partial' contributions to the property of the respective dyads. As can be seen from Fig. 3, the experimental values of ΔC_p obey Eq. (6) only in the range $F_1 < 0.8$ (in calculations $Z_{11} = 20.5$ J/mol ·K, $Z_{22} = 22.4$ J/mol ·K and $Z_{12} = 21.5$ J/mol ·K were assumed). Similar results were obtained also for series CEP (Table 2), while paucity of experimental data prevented to carry out such analysis for series CEH. Lower (as compared to additive) values of ΔC_p for copolymers in the range $F_1 > 0.8$ may be explained by the incomplete amorphization and/or by structural alterations within the amorphous phase of quenched samples. It turned out, however, that correction for the former effect (degree of crystallinity) had a minor effect, bringing the corrected points slightly closer to the theoretical curve but not eliminating the observes discrepancy. Literally, that means that the latter effect is operative.
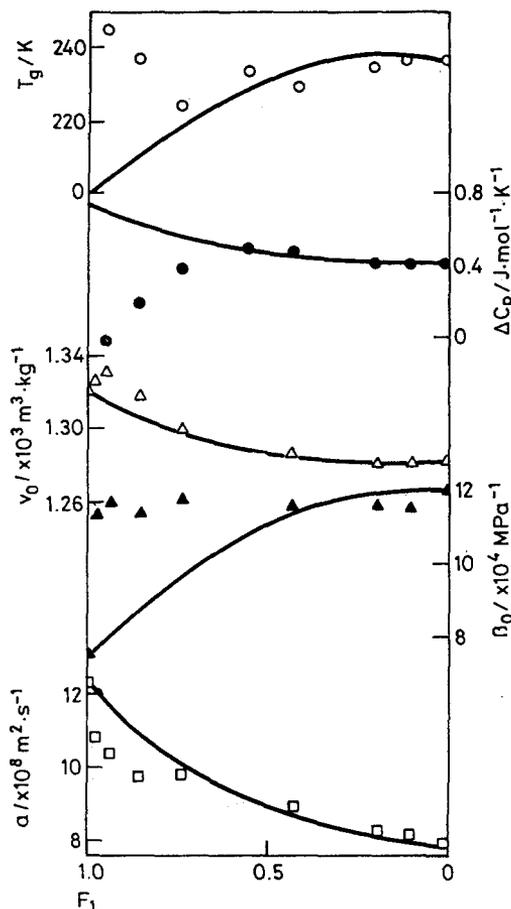
Fig. 3 Composition dependence for copolymers of series CEB of the glass transition
temperature T_g, corresponding heat capacity jump ΔC_p, melt specific volume v_g,
compressibility β_0 and thermal diffusivity a at $T=463$ K. Solid lines were calculated
using Eq. (6) and data from Table 2

A similar conclusion may be reached from comparison of experimental values
of T_g with theoretical ones which were calculated with the aid of Couchman's
equation [15]:

$$\ln T_g = \frac{f_{11}\,\Delta C_p^{11}\,\ln T_g^{11} + 2f_{12}\,\Delta C_p^{12}\,\ln T_g^{12} + f_{22}\,\Delta C_p^{22}\,\ln T_g^{22}}{f_{11}\,\Delta C_p^{11} + 2f_{12}\,\Delta C_p^{12} + f_{22}\,\Delta C_p^{22}} \tag{7}$$

As can be seen from Fig. 3 where the experimental T_g values are plotted vs. F_1
for samples of series CEB (similar data were also obtained for series CEP), the
reasonable agreement between theory and experiment is limited to the range F_1
< 0.8, while rather large positive deviations of experimental values of T_g from

theoretical curves at higher ethylene contents ($F_1 > 0.8$) should be attributed to some alterations in the structure of the amorphous phase.

Table 2

Property	Z_{11}	CEP		CEB	
		Z_{12}	Z_{22}	Z_{12}	Z_{22}
T_g / K	200	215	258	250	236
ΔC_p / J mol^{-1} K^{-1}	20.5	21.5	22.2	21.5	22.4
v_0 / $\cdot 10^3$ m^3 kg^{-1}	1.322	1.250	1.339	1.270	1.281
β_0 / $\cdot 10^4$ MPa^{-1}	7.5	12.4	10.0	12.0	12.1
a / $\cdot 10^8$ m^2 sec^{-1}	12.2	8.8	8.0	8.5	7.8
3C/p	0.87	1.8	0.84	1.8	0.84
γ_0	2.44	7.25	4.35	7.10	4.10

Properties of the melt phase

As was the case for series CEB (Fig. 3), for other series, too, at normal pressure the experimental values of the melt specific volume V_0, compressibility $\beta_0 =$ 0.0894/B and thermal diffusivity a are adequately described by an additive relationship [6] only in the range $F_1 < 0.8$ (in calculations optimum values of corresponding 'partial contributions' from Table 2 were used).

Within the temperature interval and pressure range of our measurements the experimental values of the melt specific volume of all the samples studied, V, were proved to obey the Simha-Somcynsky equation of state [13, 16]:

$$\frac{P\tilde{v}}{\tilde{T}} = [1 - 2^{1/6} y (y\tilde{v})^{1/3}]^1 + \frac{2y}{\tilde{T}} (y\tilde{v})^{-2} [1.011(y\tilde{v})^{-2} - 1.2045] \qquad (8a)$$

which is valid under the condition,

$$\left(\frac{3C}{p}\right)^{-1} [1 + y^{-1} \ln (1-y)] = \frac{y}{6\tilde{T}} (y\tilde{v})^{-2} [2.405 - 3.033(y\tilde{v})^{-2}] +$$

$$+ [2^{-1/6} y (y\tilde{v})^{-1/3} - \frac{1}{3}] [1 - 2^{-1/6} y (y\tilde{v})^{-1/3}]^{-1} . \qquad (8b)$$

In Eqs (8a) and (8b) $\tilde{P} = P/P^*$, $\tilde{T} = T/T^*$, $\tilde{v} = v/v^*$, where $P^* = C k \tilde{T}/v^*$, $T^* = q z \varepsilon^*/CK$ and v^* are characteristic reducing parameters for pressure, temperature and volume, respectively, qz is the number of external (i.e., intermolecular) contacts of the chain, z is the coordination number of a quasilattice (in ordinary practice, $z = 12$ is used), C is the number of external degrees of freedom,

ε^* is the energy parameter of the potential of intermolecular interactions, y is the fraction of occupied sites in the quasilattice, and p is the degree of polymerization.

It can be seen from Table 3 that the values of characteristic reducing parameters P^*, T^*, v^* which are determined by a standard treatment [6, 14] of experimental values of V with the aid of Eqs (8a) and (8b), are typical for non-polar carbochain polymers and reasonably well obey (Fig. 4) the following empirical correlations [17]:

$$\frac{P^* v^*}{T^*} = 1.319 - \frac{3}{2.01} T^* \cdot 10^{-4} \tag{9a}$$

$$10^{-4} T^* = \ln\left(\frac{m_0 V^*}{9.3}\right)^{2.1/3}, \tag{9b}$$

where m_0 is the molecular mass of an effective segment of the model chain which is defined as $m_0 = 2.77 \cdot 10^{-3} / (P^* v^*/T^*)$.

On the other hand, quite unusual is the composition dependence of the number of external degrees of freedom (with respect to a repeat unit of mass m in a real macromolecule), $3C/p = (P^* v^*/T^*)(3m/R)$ which may serve as a measure of the thermal mobility of polymer molecules in the melt [13]. As is evident from inspection of Fig. 5, the values of parameter $3C/p$ for samples from CEP and CEB series with nearly identical values of the parameter for the corresponding homopolymers (cf. Table 3), are satisfactorily accounted for by the additivity criterium, Eq. (6), only in the range $F_1 < 0.8$, while at $F_1 > 0.8$ significant negative deviations from additivity are observed. It is appropriate to remark here that in this latter composition range a similar variation of $3C/p$ is observed also for copolymers of the series CEH in spite of the more than twofold difference of the parameter between the respective homopolymers (0.88 for polyethylene and 2.02 for polyhexene-1). This means that the thermal mobility of macromolecules in the melt phase of all the studied copolymers in the range $F_1 > 0.8$ depends on the molar content of component 2 in the chain, rather than on its chemical nature.

Finally, we will discuss the influence of temperature, pressure and chemical composition of copolymers on their thermal conductivity in the melt state, λ, which was determined from experimental values of the heat capacity C_p, specific volume V, and thermal diffusivity a substituted into the standard formula, $\lambda = C_p a/V$. The values of λ obtained in this fashion reveal no systematic dependence on temperature in isobaric conditions, whereas in isothermal conditions one observes the typical [18, 19] fast initial increase of thermal conductivity with pressure followed by a gradual levelling-off. This behaviour was analyzed with the aid of Barker's equation [18]:

$$\frac{\Delta\lambda}{\lambda_p} = \gamma_B \, \beta_f, \tag{10}$$

where $\Delta\lambda = \lambda_p - \lambda$ is the increment of the melt thermal conductivity accompanying an increase of pressure from 0.1 MPa to P, $\beta_f = f(0.T) \, [1 - \exp(- PV_o / kT]$ is the free volume-controlled compressibility of the melt, γ_B is the quasilattice Grueneisen parameter, $f(0, T) = \exp(-1) \exp(-E_o / kT)$ is the free volume fraction of the melt at normal pressure and temperature T, V_o is the volume of one lattice site, and E_o is the energy of the hole formation in the melt.

Table 3

| Polymer	P^* / MPa	v^* / $\cdot 10^3$ m³ kg⁻¹	T^* / $\cdot 10^{-4}$ K	$3C / p$ (±10%)	γ_3
Polyethylene	850	1.2234	1.2025	0.87	2.44±0.15
CEP–02	650	1.2230	1.1450	0.82	3.33±0.64
CEP–04	555	1.2350	1.2105	0.69	4.33±0.67
CEP–10	535	1.2455	1.2225	0.63	4.14±0.76
CEP–22	635	1.1995	1.1270	0.77	3.88±0.32
CEP–43	965	1.1190	0.9265	1.50	5.00±0.31
CEP–63	750	1.1520	1.0455	1.16	5.68±0.53
CEP–68	780	1.1355	0.9560	1.24	5.61±1.23
Polypropylene	550	1.2508	1.2774	0.84	4.35±0.40
CEB–012	605	1.2230	1.1775	0.69	4.49±0.59
CEB–025	590	1.2225	1.1770	0.68	5.10±0.40
CEB–06	550	1.2170	1.1990	0.69	5.17±0.80
CEB–15	575	1.1555	1.0950	0.72	4.30±0.31
CEB–27	840	1.1195	1.0550	1.26	4.12±0.21
CEB–58	795	1.1160	1.1865	1.31	5.35±1.00
CEB–80	480	1.1885	1.2550	0.98	5.25±0.31
CEB–89	495	1.1890	1.2480	0.89	4.44±0.38
Polybutene–1	435	1.2034	1.2735	0.84	4.10±0.54
CEH–02	555	1.2305	1.2050	0.66	4.76±0.44
CEH–04	550	1.2410	1.2105	0.64	4.33±0.37
CEH–0.79	570	1.2005	1.1990	0.72	4.56±0.15
Polyhexene–1	595	1.1926	1.0765	2.02	—
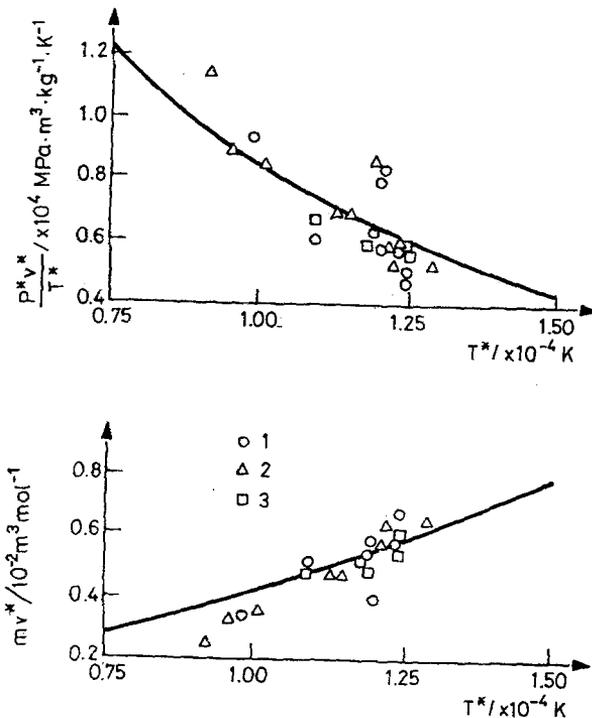
Fig. 4 Dependence of the ratio $P^* v^*/T^*$ and characteristic molar volume $m v^*$ on the characteristic temperature T^* for copolymers of series CBP (1), CEB (2) and CEH (3). Solid lines were constructed using Eqs (9a) and (9b), resp.

Values of the above parameters obtained by treatment of pertinent experimental data with the aid of Eq. (10) are also included in Table 3 (as usual [18, 19], calculations were carried out assuming a universal value, $f(0, T_g) = 0.025$ for all polymers at their respective glass transition temperatures T_g).

Once again, the calculated values of γ_B for all the studied copolymers are close to additive in the range $F_1 < 0.8$ but, contrary to the similar plot for $3C/p$, at higher ethylene contents ($F_1 > 0.8$) one observes negative (instead of positive) deviations from additivity (solid line in Fig. 5). Obviously, correlation between parameters $3C/p$ and γ_B claimed to exist for homopolymers [19, 20] does not apply for random copolymers.

It is worth noting here that the discovered deviations of thermophysical and thermodynamic properties from simple additivity, Eq. (6), of all studied series in the melt state which is presumably valid for copolymers with strictly random distribution of unlike monomers in the chain, are observed just in the composition range where the uninterrupted length of ethylene sequences proved sufficient for their crystallization. It follows therefrom that in respect of chain microstructure
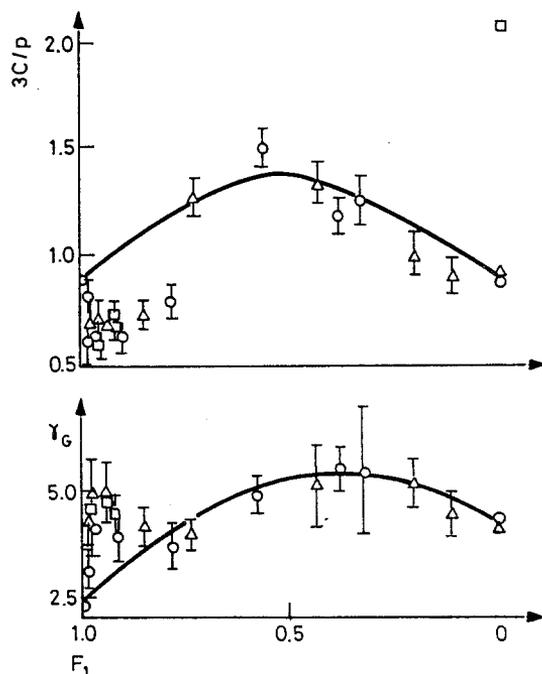
Fig. 5 Composition dependence of the number of external degrees of freedom per chain repeat unit, $3C/p$, and of the quasilattice Grueneisen parameter, γ_g, for copolymer melts. Solid lines were construted using Eq. (6)

the distribution of unlike monomers in the copolymer chains, at the dyad level at least, is not truly random. In other words, in that composition range the macromolecules consist of sufficiently long, continuous ethylene sequences 'diluted' with moieties of different chemical nature.

Conclusions

The results presented in this paper are consistent with the following conclusions. The higher reactivity of ethylene compared to other comonomers is the primary cause of a microblock chain structure of copolymers of all series in the range $F_1 > 0.8$ where the chains are composed of sufficiently long, continuous ethylene sequences randomly interrupted by monomeric moieties of different chemical nature. In this composition range the properties of the melt phase depend on the relative content of comonomers rather than on their chemical nature, while the latter exerts an appreciable influence on the crystallizability of ethylene sequences, namely: at identical molar compositions the degree of crys-

tallinity is diminished and the melting temperature of the crystalline phase of copolymers is lowered, as the molecular structure of a comonomer becomes more complex. This effect becomes weaker when the molar content of ethylene is smaller, so that in the composition range $F_1 < 0.8$ the properties of copolymers of all series obey the standard additive rules for random copolymers.

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Zusammenfassung — Durch Messungen der Wärmekapazität im Temperaturintervall 140–480 K und des spezifischen Volumens im Temperaturintervall 330–490 K und im Druckbereich 27.8-100 MPa wurden Random-Kopolymere von Ethylen und Propylen, Buten-1 und Hexen-1 charakterisiert. Die Analyse der Abhängigkeit des Kristallinitätsgrades, der Schmelz- und Glasumwandlungspunkte sowie der thermodynamischen und thermophysikalischen Eigenschaften der Schmelzen führte zu einem Schluß über die Mikroblock-Struktur von Makromolekülen aller Serien bei einem molaren Ethylengehalt von $F_1 > 0.8$. In diesem Zusammensetzungsintervall scheinen die Eigenschaften des Kopolymers unabhängig von der chemischen Natur des Komonomers zu sein, im Gegensatz zum festen Zustand, wo bei einer ähnlichen molaren Zusammensetzung sich der Kristallinitätsgrad verringert und die Schmelztemperatur sinkt, wenn die Molekülstruktur des Komonomers komplexer wird. Dieser Effekt wird kleiner, wenn F_1 abnimmt, so daß im Zusammensetzungsbereich mit $F_1 < 0.8$ die Eigenschaften der Kopolymere aller Serien additiv sind.