Determination of the Degree of Crystallinity of Graft Copolymers of Styrene with ϵ-Caprolactam by a Calorimetric Method and Investigation of Their Thermal Stability

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Abstract

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Determination of the Degree of Crystallinity of Graft Copolymers of Styrene with ϵ-Caprolactam by a Calorimetric Method and Investigation of Their Thermal Stability

Electron-microscopic and structural studies in recent years have shown that the process of polymer crystallization is complex and leads to the formation of various structural forms (globules, bundles, ribbons, spherulites, dendrites, single crystals), depending on the structure—in particular, the regularity and flexibility—of the macromolecules and on the conditions of polymer crystallization ([1–8]). At the same time, many properties of crystalline polymers depend on their supramolecular structures and degree of crystallinity ([9–14]).

As we have already reported ([15]), by the method of chemical molding we obtained graft copolymers of ϵ-caprolactam with styrene, taken in different ratios.

It seemed of interest to us to investigate the thermal stability and degree of crystallinity of these copolymers as a function of composition. For this purpose it proved possible to use the method of differential thermal analysis.

As is known, melting of crystalline polymers occurs within a small temperature interval and is accompanied by an abrupt change in volume and heat capacity, and takes place with absorption of heat. Polymer melting may be regarded as a diffuse first-order transition ([16]).

In the present work, the melting and decomposition temperatures were determined according to the procedure described earlier ([17]), using a Kurnakov pyrometer with simultaneous recording of the change in weight during heating. The results obtained are presented in Table 1. As is seen from the data of this table, when the styrene content in the copolymer is varied from 10 to 50%, the thermal stability of the copolymers does not change, and decomposition (including that of the completely "cross-linked" sample) occurs in the temperature interval of degradation of polystyrene and polycaproamide.

Table 1

Figure 4

Figure 1: Figure 4

Figure 3

Figure 2: Figure 3

Thermographic study of copolymers of styrene with ϵ-caprolactam

Composition of copolymer: styrene/ϵ-caprolactam, wt. %	Amount of catalytic system, mol. % relative to ϵ-caprolactam	Average mol. weight of one branch**	Flow temperature from thermomechanical data, °C	Decomposition onset temperature, °C	Amount of heat absorbed during melting, cal/g	Degree of crystallinity, %	Density, g/cm^3
0 : 100	0.40	–	230	352	17.8	41.4	1.149
10 : 90	0.28	45 000	220	340	–	–	–
20 : 80	0.40	27 000	225	347	8.6	20.0	1.081
33 : 67	0.54	20 000	225	340	5.7	13.4	1.070
33 : 67*	0.80	–	214	340	–	–	–
50 : 50	0.70	10 000	220	340	2.4	5.6	1.048
100 : 0	–	–	90	316	0	0	1.035

* Sample insoluble in cresol (completely cross-linked).
** Calculated according to (^{15}).

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Fig. 4. X-ray diffraction patterns of copolymer samples:
1 –polycaproamide; 2 –copolymer containing styrene and ϵ-caprolactam in a ratio of 20 : 80 (by weight); 3 –polystyrene

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Fig. 3. X-ray diffraction pattern of amorphous (a) and crystalline (b) polyvinyl oleate

As was established earlier (^15), the copolymers studied have a three-dimensional structure. However, there is still no sufficiently definite conception of the nature of the cross-links. Wichterle and Gregor (^18) attribute their formation to condensation of the Kleisen type. The results obtained by us show

Fig. 1

Figure 3: Fig. 1

Fig. 2

Figure 4: Fig. 2

that the strength of the cross-links is of the same order as that of the main bonds in the macromolecule.

The method of differential thermal analysis was also used by us to estimate the degree of crystallinity of the graft copolymers named.

The usual methods for determining crystallinity (X-ray, by density, by heat capacity) are rather complicated and cannot always be applied.

From examination of the thermomechanical curves of the copolymers studied (Fig. 1) it is seen that their glass-transition temperatures lie in the temperature range 100-120°, and the transition to the fluid state occurs at 220-230°.

Fig. 1. Thermomechanical compression curves of graft copolymers of styrene and ϵ-caprolactam, containing styrene (in wt. %):
1 –0; 2 –20; 3 –33; 4 –50; 5 –100

Decomposition (accompanied by absorption of heat) begins approximately 100-140° above the melting point of the crystalline phase, both for the copolymer containing 20 wt. % styrene and for poly-ϵ-caproamide (Fig. 2).

Determination of the heats of melting of the polymers was carried out in a special block (calorimeter) with diathermic jackets according to Kapustinskii–Barskii (⌢19, ⌢20), with an accuracy of 5%. In an aluminum block with cylindrical jackets of penoceramic, the polymer under study and the standard–aluminum oxide–in amounts of 0.03-0.05 g were placed in stainless-steel cups. The heat entering the specimen through the diathermic jacket is monitored by measuring the temperature gradient of batteries of consecutively connected copper-constantan thermocouples. With uniform heating at a rate of 2.0 degrees per minute, a quasi-stationary regime is established after several minutes. The emf of the differential thermocouple is recorded by an EPP-09 with a scale of $3 \cdot 10^{-3}$ mV. The area of the peak of the curve recorded by the EPP pen is proportional to the heat of the phase transition $m\Delta H = kS$, where ΔH is the heat of transformation, S is the area,

Fig. 2. Curves of weight loss $(1', 2', 3')$ and of differential change in temperature (1, 2, 3) of polymers:
1, $1'$ –poly-ϵ-caproamide; 2, $2'$ –graft copolymer containing styrene and caprolactam in the ratio 20 : 80 (by weight); 3, $3'$ –polystyrene

Fig. 3. Change in the amount of heat going into melting of the crystalline phase, for copolymers of composition:

Fig. 3

Figure 5: Fig. 3

1 —polycaproamide; 2 —styrene : ϵ-caprolactam (20 : 80); 3 —styrene : ϵ-caprolactam (33 : 67); 4 —styrene : ϵ-caprolactam (50 : 50)

k is the instrument constant. The instrument was preliminarily calibrated using substances with known heats of phase transitions (benzoic acid and potassium nitrate).

As the amount of styrene contained in the copolymer increases, the heat of the phase transition decreases (Fig. 3), i.e., the crystallinity decreases, but melting occurs in one and the same temperature interval. A qualitative study of the copolymers by the X-ray structural method gives an analogous picture (Fig. 4). It is evident that the decrease in the amount of crystalline phase in the copolymer is due to a decrease in the amount and molecular weight of poly-ε-caprolactam grafted to the amorphous carbon-chain initiator. It should be noted that the decrease in the degree of crystallinity of the copolymers does not occur in direct proportion to the decrease in the content of the polyamide portion, but much more sharply. This is evidently connected with difficulties in ordering the polyamide branches under these conditions.

The degree of crystallinity of the copolymers was determined from the amount of heat absorbed during melting of the crystallites, according to the formula $G = 2.33Q$, where G is the degree of crystallinity (%), and Q is the heat of fusion (cal/g). The coefficient 2.33 was determined empirically from the heat of fusion and degree of crystallinity of poly-ε-caprolactam (the degree of crystallinity of poly-ε-caprolactam was determined from density on the basis of data obtained by Wichterle et al. ([21])). The obtained data are given in Table 1. They agree well with the data obtained by us by density measurement.

Thus, the method described can evidently, in principle, be used to determine the degree of crystallinity of various graft and, possibly, block copolymers. The formula given, in its present form, is suitable for calculating the crystallinity of any graft copolymers of ε-caprolactam with amorphous co-components. In the case of other starting reagents, only the coefficient must be changed.

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