

辐射交联聚合物的结晶动力学

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摘要 电离辐射在工业上应用的基础是聚合物的辐射交联,它们是绝缘电线和电缆的交联,热收缩性材料的生产,泡沫塑料等等。辐射引发交联已经被广泛地研究,特别是凝胶的形成和聚合物结构、辐照条件对交联度的影响。对于一般法和辐射法交联的聚合物却很少有人研究它的结晶过程。例如,已经证明除了在非常高的吸收剂量外,辐照的聚乙烯中总的结晶度不受影响,但对于聚丙烯和聚丁烯在凝胶点剂量时,它们的结晶度大大减少。辐照聚合物的重新熔融,进一步减少了总结晶度。

本工作表明不仅总的结晶度而且结晶动力学也受辐射引发交联的影响。结晶速率指出结晶划分成二种不同增长机理的过程。冷却速率是一个重要的因素,它决定结晶过程并影响与交联的半晶聚合物的结晶度和形态有关的其它性质。

关键词 电离辐射;辐射交联;交联度;结晶度。

CRYSTALLIZATION KINETICS OF RADIATION CROSSLINKED POLYMERS

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SUMMARY

Several industrial applications of ionizing radiation are based on radiation crosslinking of polymers: crosslinking of wire and cable insulation, production of heat shrinkable materials, plastic foam, etc. Radiation induced crosslinking has been the subject of many studies, especially the gel formation and effect of polymer structure and irradiation conditions on the yield of crosslinks. Much less has been done to study crystallization of crosslinked polymers in general and radiation crosslinked polymers in particular. It has been shown, for example, that the total crystallinity in irradiated polyethylene is not affected, except at very high absorbed doses. On the other hand it is significantly reduced in polypropylene and poly-1-butene already at doses

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about the gel point. In all cases remelting of irradiated polymers further reduced the total crystallinity.

In this work it is shown that not only the total crystallinity, but also the crystallization kinetics are affected by radiation induced crosslinks. The rate of crystallization indicated that the crystallization can be separated in two processes with different growth mechanisms. The rate of cooling is an important factor which determines the crystallization procedure and affects other properties dependent on crystallinity and morphology of crosslinked semicrystalline polymers.

KEY WORDS Ionizing radiation; Radiation crosslinking; Yield of crosslinks; Crystallinity.

INTRODUCTION

Crystallization kinetics of polymers has been the subject of numerous studies (1). The crystallization kinetics of crosslinked polymers and in particular of radiation crosslinked polymers has been studied to a significantly lesser extent. Most of the published data deal either with melting behaviour or with the structure of irradiated polymers. It was shown (2, 3) for example, that supermolecular structures crystallization behaviour of irradiated polyethylene change significantly. This subject is of increasing interest due to continuously expansion of industrial applications based on radiation crosslinking of polymers.

On irradiation, several processes occur concurrently in polymers: crosslinking, molecular scission, change of unsaturation and formation of small amount of gases, mainly hydrogen. The relative significance of these processes depends mainly on the type of polymer, irradiation conditions and to some extent also on supermolecular structure. It is well established that polyethylene crosslinks easily, while polypropylene mainly degrades on irradiation (4). Irradiation of polymer melts results in the formation of homogeneous network structure, while irradiation of solid semicrystalline material produces an inhomogeneous structure, since almost all crosslinks occur in the amorphous phase or at the surface of crystalline phase (5). Practically no crosslinks are formed within the boundaries of crystalline regions and the effect on supermolecular structure of polyethylene is negligible up to very high levels of absorbed dose, of the order of several thousands of kGy. The significant change in supermolecular structure was observed, however, when irradiated polyethylene was melted and recrystallized.

The subject of this work was to study the crystallization of several types of polymers irradiated in semicrystalline state. The special emphasis was given to kinetics of crystallization of polymers melted after irradiation. The differential scanning calorimetry (DSC) technique was used to study crystallization kinetics. The nonisothermal or dynamic crystallization technique was preferred for this study, as compared to more often applied isothermal crystallization technique. This technique was used successfully for the study of crystallization of noncrosslinked polyethylene (7) and is believed to be closer to many actual polymer processing conditions.

EXPERIMENTAL

Materials.

The following materials were selected for this study: high density polyethylene,

NBS 1475 (National Bureau of Standards reference material, NBS, USA), low density polyethylene (LDPE), Lothrene 0302 (Cdf Chimie, France), linear low density polyethylene (LLDPE), Dowlex 2552 (Dow Chemical Co., USA) and isotactic polypropylene (PP), (Aldrich Chem. Comp., USA).

Irradiation.

All irradiations were carried out at Co-60 gamma source; in argon atmosphere, at room temperature and absorbed dose rate of the order of about 5 kGy/h. All samples were prepared in the following way: polymer was melted and pressed in plates about 5 mm thick. The circular shapes were cut and encapsulated in DSC aluminum pans, in which irradiation was performed.

Calorimetry.

Differential scanning calorimeter (DSC), DSC-2, Perkin Elmer, USA, was used for the study of crystallization kinetics. Samples of 5-10 mg were prepared as described. After irradiation, samples were remelted in DSC. Before any crystallization run, the sample was held for 10 minutes at temperature about 20 degrees above melting temperature in order to destroy any traces of previous crystallinity. The crystallization was performed at cooling rates 2.5, 5, 10 and 20 deg/min from the starting temperature to 320 K. The crystallization exotherms were recorded, digitized by a graphic digitizer and all calculations done on a small computer system. Experimental results were presented as plots of % of crystallinity in the function of time, and further analyzed according to Avrami plot of $\log(-\ln(1-X))$ versus $\log(\text{time})$. The heat of crystallization, time required to reach 50% of total crystallinity, the Avrami exponent were calculated in a usual way for these parameters. The crystallization temperature was determined as that point which corresponded to the maximal deviation from the base line on crystallization exotherm. It can be interpreted as the temperature of the maximal rate of crystallization, i. e. the temperature (and time) at which growing fronts of crystals impinge one on another (7).

RESULTS AND DISCUSSION

Figure 1 shows the crystallization exotherms for different materials and several absorbed doses near or above the gel point. For all materials studied here the shift of crystallization exotherms to lower temperatures (higher undercooling for crystallization) was observed. In addition all three different types of polyethylenes studied here exhibit the appearance of double maxima endotherms at the absorbed doses above the gel point. This behaviour indicates that the presence of crosslinks affects the crystallization procedures in irradiated samples, besides inhibiting the overall degree of crystallinity. It can be postulated that in noncrosslinked or slightly crosslinked materials chain folding dominates the crystallization mechanism while highly crosslinked materials crystallize according to micellar model. The same effect was reported earlier (3) in the case of melt irradiated high density polyethylene and was observed by X-ray analysis. In highly crosslinked sample (HDPE, 1450 kGy) again only one maximum was observed indicating the domination of micellar crystallization.

Figure 2 shows the heats of crystallization for different absorbed doses. The values correspond to the primary crystallization only, but due to some ambiguity in separating

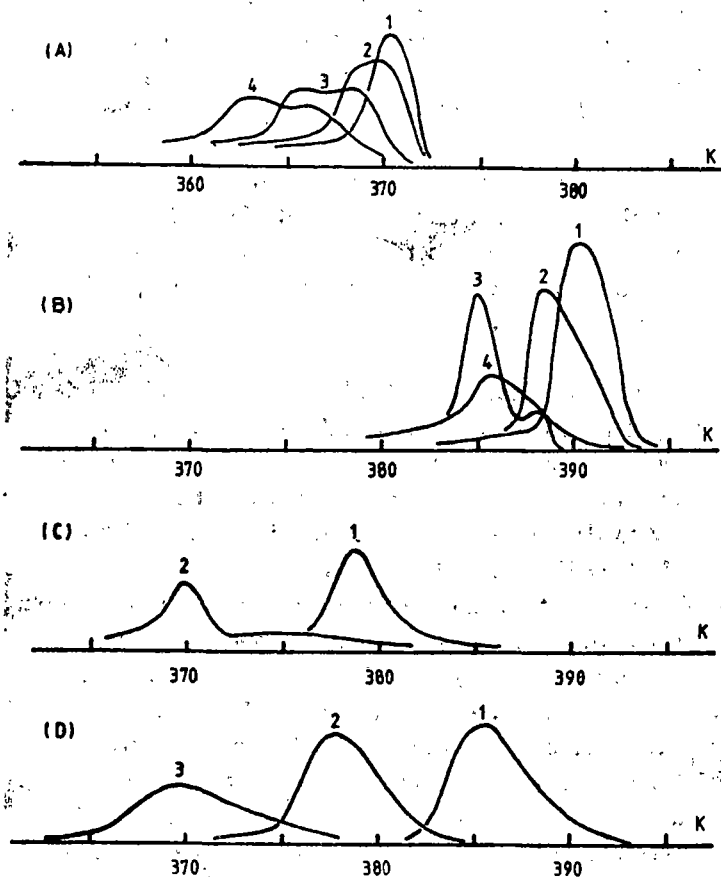


图 1 DSC 结晶放热, 在冷却速率 5 K/min 时的动态结晶

Fig. 1 DSC crystallization exotherms. Dynamic crystallization at cooling rate 5 K/min.

- (A) - LDPE, 1- unirradiated, 2- 100 kGy, 3- 200 kGy, 4- 500 kGy.
 (B) - HDPE, 1- unirradiated, 2- 200 kGy, 3- 500 kGy, 4- 1450 kGy.
 (C) - LLDPE, 1- unirradiated, 2- 500 kGy.
 (D) - PP, 1-unirradiated, 2- 500 kGy, 3- 1000 kGy.

it from secondary crystallization they are interpreted with some precaution. It is obvious that the heat of crystallinity is significantly reduced in HDPE and PP, but almost unaffected in LDPE and LLDPE. Apparently the crosslinks add relatively little imperfections to already highly branched structures of LDPE and LLDPE while in linear HDPE presence of crosslinks significantly change the conditions of crystallization due to increased level of branching points. The decrease of the crystallinity in PP cannot be explained in terms of crosslinks. It is probably due to overall molecular degradation, although some crosslinks may also act as inhibitors for crystallization procedure. Within the experimental error the heats of crystallinity (and overall crystallinity) do not depend on the cooling rate.

Figures 3-5 show the crystallization temperatures in the function of cooling rates, for different absorbed doses, for LDPE, HDPE and LLDPE, respectively. Figures 6-7 show half times of crystallization in the function of absorbed dose for different

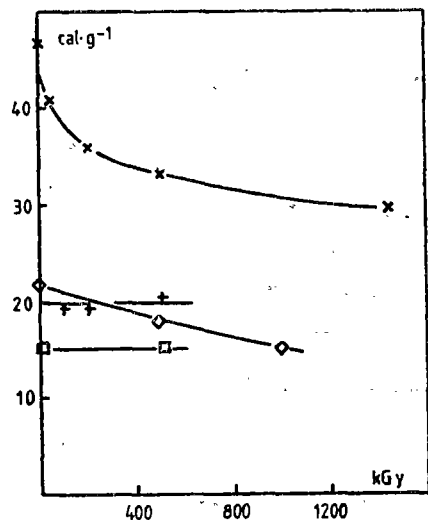


图2 结晶热与吸收剂量的关系
Fig. 2 Heat of crystallization in the function of absorbed dose.
LDPE(+), HDPE(x), LLDPE, (□), PP(◇).

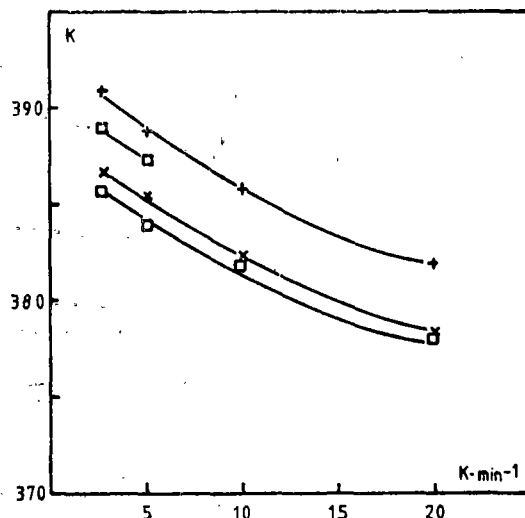


图4 结晶温度与冷却速率的关系
Fig. 4 Crystallization temperature in the function of cooling rate.
HDPE. Unirradiated (+) 200 kGy (x), 500 kGy(□), 1450 kGy(◇, ◇)

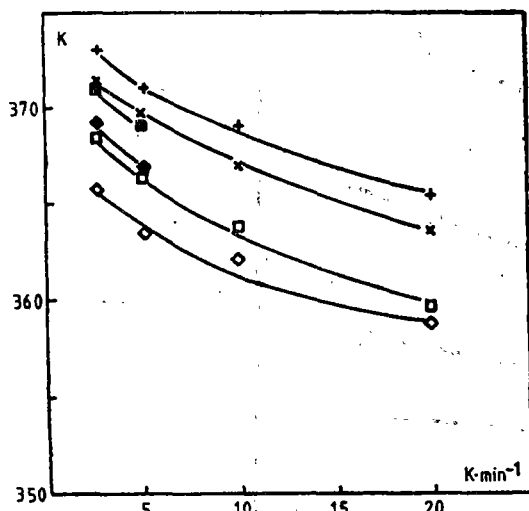


图3 结晶温度与冷却速率的关系
Fig. 3 Crystallization temperature in the function of cooling rate.
LDPE. Unirradiated(+), 100 kGy(x), 200 kGy(□, ■), 500 kGy(◇, ◇)

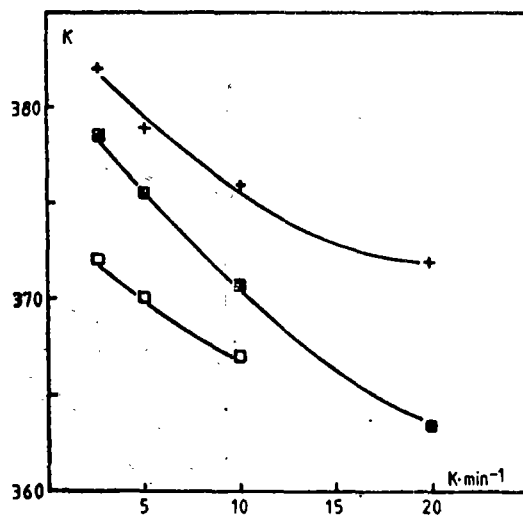


图5 结晶温度与冷却速率的关系
Fig. 5 Crystallization temperature in the function of cooling rate.
LLDPE. Unirradiated(+), 500 kGy (□, ■)

cooling rates. As expected, the crystallization temperatures decrease with increase of cooling rates, but also with absorbed dose. The half life of crystallization increases with absorbed dose. The effect is more pronounced at low cooling rates and negligible at higher cooling rates.

The attempts to use approach described by Ozawa (8) to calculate the Avrami exponent for heterogeneous nucleation conditions from nonisothermal crystallization,

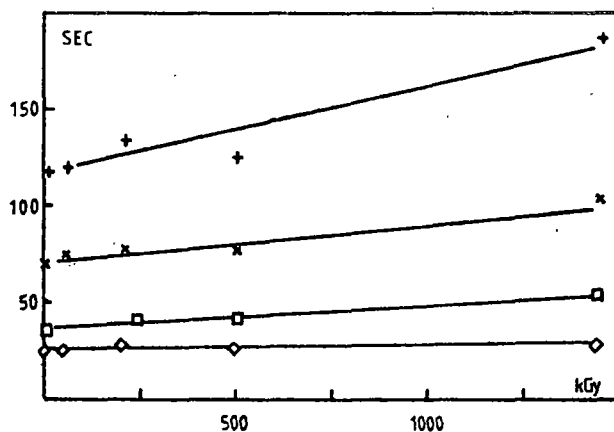


图 6 不同冷却速率下动态结晶半衰期与吸收剂量的关系
 Fig. 6 Half time of dynamic crystallization in the function of absorbed dose, at different cooling rates.
 HDPE. 2.5 K/min(+), 5 K/min(x), 10 K/min(□), 20 K/min(◇).

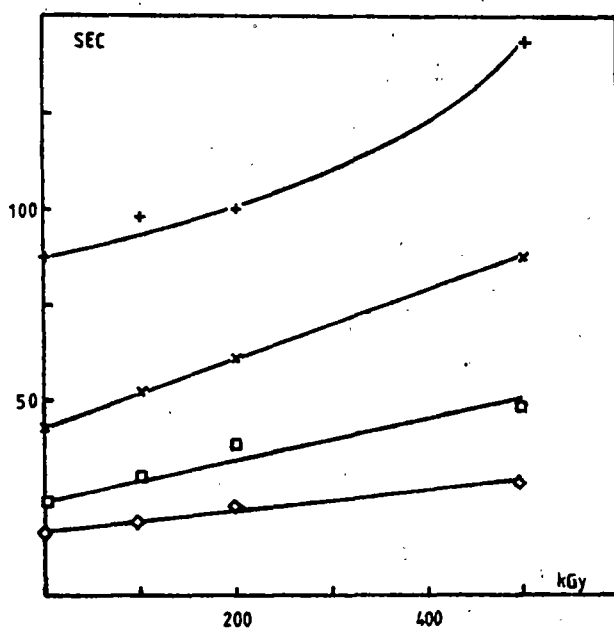


图 7 在不同冷却速率下, 动态结晶半衰期与吸收剂量的关系
 Fig. 7 Half time of dynamic crystallization in the function of absorbed dose, at different cooling rates.
 LDPE. 2.5 K/min (+), 5 K/min(x), 10 K/min(□), 20 K/min(◇).

was not successful, since linear dependence between the cooling rate and Avrami ordinate was not obtained. Instead, the Avrami exponent was calculated in a usual way. In that case, it can be assumed that due to continuous increase of supercooling, the number of nucleation centers increases with time. Therefore, the Avrami exponent

should be greater by one unit than the equivalent exponent corresponding to isothermal crystallization conditions. This was actually observed, the values between 3 and 4 were calculated for materials studied. The deviations of Avrami exponent from integer values have been many times reported in literature and it is not surprising that it was common behaviour for dynamically crystallized samples in this work. In irradiated samples additional complication in applying the Avrami equation arises from the fact that two different slopes were observed in almost all samples. It can be concluded that this type of analysis of dynamic crystallization data in radiation crosslinked samples has a very limited value.

In conclusion, it may be said that the kinetic analysis of crystallization by non-isothermal DSC can provide very useful informations about crystallization procedures and change of crystallization procedures from noncrosslinked to highly crosslinked materials. The crosslinking strongly influence the crystallization behaviour, rates and temperatures. At the low degrees of crosslinking two different crystallization procedures may take place in the same polymer, one after the other. The two processes are clearly separated on time/temperature scale and can be easily identified by DSC. It has been postulated that the chain folding dominates in noncrosslinked or slightly crosslinked polymers and occurs very fast at low undercoolings. In crosslinked polymers the micellar crystallization takes place at larger undercoolings. The properties dependent on crystallinity and crystalline structure of polymers should be affected accordingly.

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