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THE EFFECT OF COOLING RATE DURING CRYSTALLIZATION ON THE MELTING BEHAVIOR OF POLYPROPYLENES OF DIFFERENT CHEMICAL STRUCTURE

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Abstract. The melting behavior of polypropylenes of different chemical structure (isotactic homopolypropylene, propylene-based block and random copolymers and maleic anhydride grafted polypropylene) was studied by differential scanning calorimeter (DSC) and optical microscopy. Melting behavior and the crystal structure of polypropylene and its copolymers were observed depending on the crystallization rate, chemical nature of co-monomer unites and regularity of co-monomer units arrangement in the polypropylene main chain.

Keywords: polypropylene, melting, crystal structure, DSC, microscopy.

1. Introduction

Polypropylene and its copolymers are the most important commodity thermoplastic polymers which are found in a wide variety of applications due to its excellent strength, toughness, high chemical resistance and high melting point. Polypropylene versatility along with its low cost and technological potentials has rendered it one of the most used materials worldwide [1-5].

Isotactic homopolypropylene (PP) is a crystalline polymer whose properties are dependent on the degree of crystallinity and it exhibits three crystalline forms: the monoclinic α-phase, the hexagonal β-phase, and the orthorhombic γ-phase [6-10]. When PP is formed, its crystal formation changes according to the heat treatment temperature and the conditions of cooling process. These changes create differences in strength, heat resistance and pressure bonding properties. Accordingly, it is interesting and important to find out how to manage the structure of the polymer by varying the crystallization conditions during processing.

Propylene-based block copolymer (bPP) is a chain of molecules of propylene gap in the chain of ethylene copolymer. Propylene block copolymers are produced in the form of homogeneous color granules with high impact strength (at low temperatures) and high flexibility; increased long-term thermal stability; resistance to oxidative degradation during production and processing of polypropylene as well as of the product based on it. Owing to the crystalline structure the polypropylene block copolymer is a thermoplastic polymer [11-12].

Propylene-based random copolymers (rPP) are made by copolymerizing propylene and small amounts of ethylene (usually up to 7 wt %) and their structure is similar to isotactic polypropylene, but the regular repeating of propylene units along the macromolecular chains is randomly disrupted by the presence of the comonomer ones. The presence of ethylene units reduces the melting point and crystallinity by introducing irregularities into the main polymeric chain. The advantages of this class of polymers are improved transparency, relative softness, lower sealing temperature, and moderate low-temperature impact strength due to the lowered glass-transition temperature [13-15].

Maleic anhydride grafted PP (mPP) is the most common functional adhesion promoter. It was proved to be effective functional molecule for the reactive compatibilization [1, 16-18].

It is generally known that the properties of semi-crystalline polymers depend strongly on the size and shape of their supramolecular structure [1, 16, 19, 20]. The purpose of this paper is to present new results concerning the melting behavior and the crystal structure of polypropylene and its copolymers depending on the crystallization rates, chemical nature of co-monomer unites and regularity of co-monomer units arrangement in the polypropylene main chain.

2. Experimental

2.1. Materials and Sample Preparation

All polymers used in this study are commercially available. The isotactic homopolypropylene iPP – Caplen 01030, melt index 1.2 g/10 min; the propylene-based random copolymer rPP – SEETEC R3400, content of ethylene groups 3 wt %, melt index 8 g/10 min; the propylene-based block copolymer bPP – SEETEC M1400, content of ethylene groups 9 wt %, melt index 8 g/10 min, the maleic anhydride grafted polypropylene mPP – Polybond 3002, content of polar groups 0.6 wt %, melt index 12 g/10 min.

2.2. DSC Measurements

DSC measurements were made on DSC thermal system Microcalorimeter DSM-10ma. Its temperature scale was calibrated from the melting characteristics of indium. The experiments were conducted in non-isothermally mode. The sample was first heated up to 473 K and maintained at this temperature for 10 min in order to erase any previous morphological history which the sample might be carrying. The sample was then non-isothermally crystallized when it was cooled down to room temperature at different cooling rates (1, 2, 4, 8, 16, 32, 64 K/min). It was subsequently heated at the heating rate of 8 K/min. The sample was then repeatedly non-isothermally crystallized with the same cooling rates to permit structure microphotographs. The samples were approximately 7 mg. All curves were normalized to the unit weight of the sample.

The percent crystallinity, X_c, of the samples is calculated by [21]:

$$X_c = \Delta H_m / [\Delta H_{m0}]$$

where ΔH_m and ΔH_{m0} are melting enthalpy of a sample and 100% crystalline PP (147 J/g [22]), respectively.

2.3. Microscopy

The Axio Imager microscopes Z2m (Collective use center "New materials and technologies", IBCP RAS) with Transmitted-light differential interference contrast (TL DIC) was used to obtained microphotographs.

3. Results and Discussion

The influence of crystallization rate on melting behavior of PP and copolymers were investigated. The melting endotherms of PP and its copolymers after various crystallization rates are presented in Fig. 1. Henceforth, for all investigated polymers, the peak at the lower temperature is called peak-1, and at the higher temperature is called peak-2. The values of melting temperature T_m and crystallinity X_c are listed in Table.

Fig. 1a shows the corresponding DSC thermographs of the samples PP recorded after cooling with different rates. It can be seen from Fig. 1a that melting behavior depends remarkably on the cooling rate. At lower crystallization rates – 8 K/min, the general feature of the DSC curves is the single melting peak localized mainly at the temperature of about 436 K. With increase of cooling rate one melting peak transformed into double melting peaks. At crystallization rate of 8 K/min on the DSC melting curves there appears shoulder peak at about 438 K, which grows into a complete peak-2 at the crystallization temperature 32 K/min and 64 K/min, whereas the position of the peak-1 is displaced at the location of lower temperature 434 K. Such dependence is explained by the formation of more advanced and stable crystal structures at low cooling rate, whereas with increasing cooling rate supercooling increases and a large amount of defective crystals are exposed to reorganization and recrystallization during heating process.

Thermal parameters of polymers samples during melting process after different crystallization rates

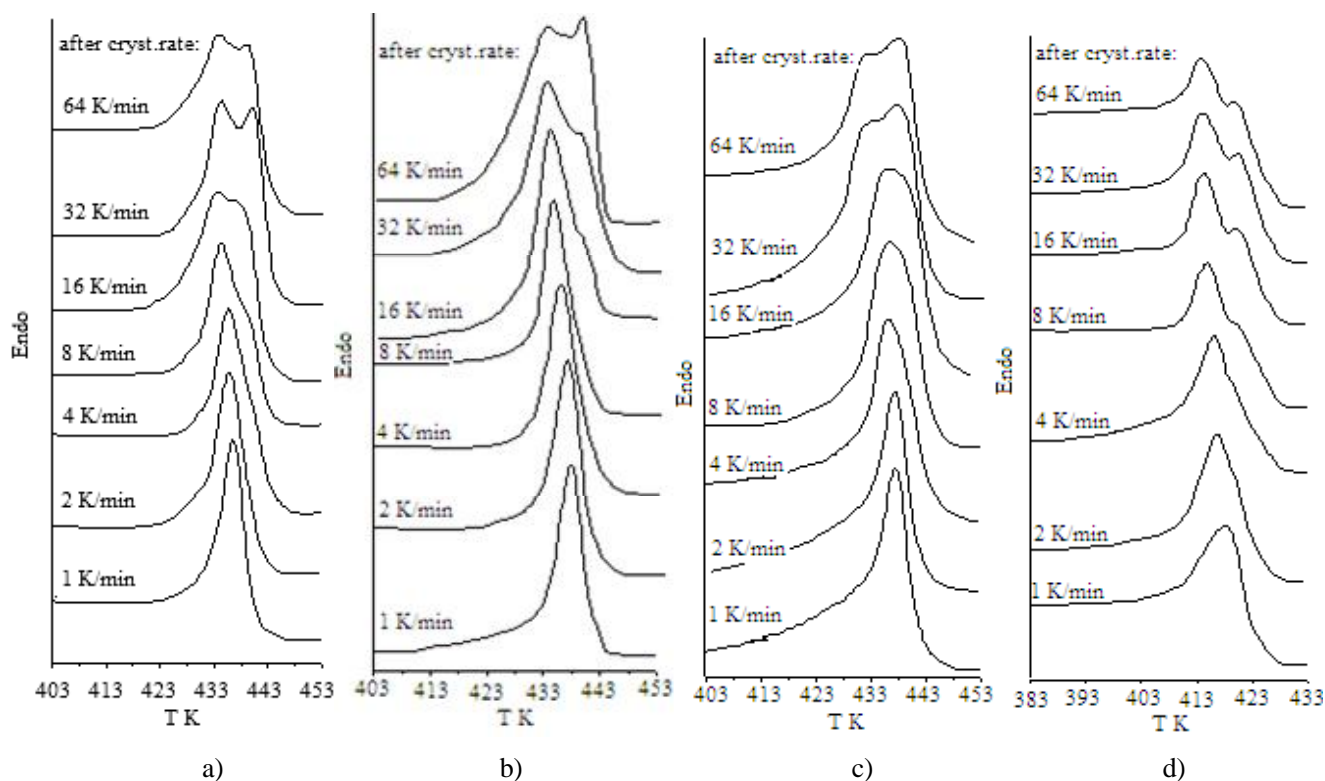| Sample	Cryst. rate, K/min	T_m, K	X_c, %	Sample	Cryst. rate, K/min	T_m, K	X_c, %
PP	64	434, 439	50	mPP	64	433, 439	63
	32	434, 439	49		32	433, 439	62
	16	433, 438	46		16	434, 439	49
	8	434	47		8	435	54
	4	435	49		4	436	53
	2	439	54		2	437	55
	1	436	58		1	438	63
bPP	64	433, 439	62	rPP	64	413, 420	31
	32	433, 438	60		32	413, 420	29
	16	436, 439	59		16	414, 421	29
	8	436	60		8	415, 420	29
	4	436	61		4	416, 420	25
	2	437	63		2	417	25
	1	438	63		1	418	26

Fig. 1. DSC thermograms of samples at 8 K/min heating: PP (a); mPP (b); bPP (c)
and rPP after crystallization with different rates (d)

In Fig. 1b mPP samples show melting endotherms after different crystallization rates. As well as pure PP, the DSC curve for mPP shows single melting peak under low cooling rate. It should be noted that appearance and increases of shoulder peak for such copolymer is observed at higher cooling rates – 16 K/min. Another distinguishing feature of mPP melting after different crystallization rates is significant decrease of melting temperature of peak-1 (from 438 K after cooling rate 1 K/min to 433 K after cooling rate 64 K/min).

Fig. 1c represents the heating DSC thermographs for the bPP samples prepared also at various cooling rates. Curves have the similar character described above by maintaining the main polypropylene chain under the block introduction of ethylene units. This later transition from a single peak to a double peak can be explained in terms of polypropylene chemical structure change by the introduction of functional groups. Since the regular introduction of functional groups decreases mobility of the system and increases the viscosity of the system, at low cooling rates this leads to the rapid formation of crystallization centers around them to form more perfect crystals than in pure PP. This displayed the higher melting temperatures of mPP and bPP. In the transition to higher cooling rates of up to 16 $^{\circ}$/min, at which the viscosity increases, the rearrangement of molecules copolymers is difficult, which in turn reduced the rate of crystallization,

resulting in the formation of qualitatively less perfect package. The melting temperature T_m decreases by 5 K. A further increase of the material crystallization rate contributes to recrystallization and formation of amid bulk imperfect crystals a high-melting crystalline structure.

The statistical introduction of ethylene units into the main polypropylene chain affects greatly the crystalline structure of rPP in Fig. 1d. Firstly, a decrease in the melting temperature of the polymer matrix of about 293 K is observed. Secondly, the peak-2 as a shoulder peak appears at the crystallization rate of 4 K/min. For the propylene-based random copolymer the ethylene-mono-mers are often considered as a defect points in polypropylene matrix. This induces structure heterogeneity in the long chains of polypropylene namely short propylene sequences leading to a decrease in crystallizable sequence length. Even small co-monomer content (3 %), as in our case, results in short crystalline sequence.

From the Table one can observe the relationship between the crystallization rate and crystallinity of polymers samples. Comparing the crystalline degree of the samples at a rate of crystallization (for example 1 K/min) one can note that the regular introduction of the co-monomer units of any chemical nature (mPP and bPP) leads to an increase in the polypropylene crystalline degree by 5 %. Such incorporated co-units are not defect points, they lead to the facilitating folding crystalline

structure. Due to the described above statistical distribution of ethylene co-units (defect points in the propylene random copolymer rPP), the crystallinity decreases by 30 %. On the other hand, crystalline degree of PP, mPP and bPP is characterized by decrease with increase crystallization rate, followed by crystallization increase at higher rates (32 K/min and 64 K/min). Samples of rPP are characterized by the constancy of crystalline degree at low cooling rates and its growth of 4–5 % even at the cooling rate of 8 K/min. These dependences as well as formation of the shoulder and peak-2 on the DSC thermograms are explainable in terms of reorganization and recrystallization of the polypropylene supramolecular structure.

The described above crystalline structures of PP, mPP, bPP, and rPP obtained after different crystallization rates were visualized by microscopy. Fig. 2 shows microphotographs of PP, mPP, bPP, and rPP obtained after different cooling rates.

For all polymer samples in the train of crystallization the line radial bundles emanating from a single point – polypropylene crystalline structure – are formed. The crystalline sizes of the samples vary widely depending on the polymer crystallization rate and its chemical structure. At higher cooling rates and structural inhomogeneity of the propylene long chains in random copolymer formed submicroscopic crystal structures – finely-grain-like structure. Crystallization at lower cooling rates leads to the formed crystals in diameter of about 100 microns. It is necessary to note that the size and shape of the supramolecular structures have great influence on the mechanical properties of the polymer. Samples with finely-grain-like structure have high strength and good elastic properties. Elasticity loss of crystalline polymers is manifested in the appearance of cracks and breaks at the crystals interface. The increase of its size leads to the fragility increased and decrease of strength.
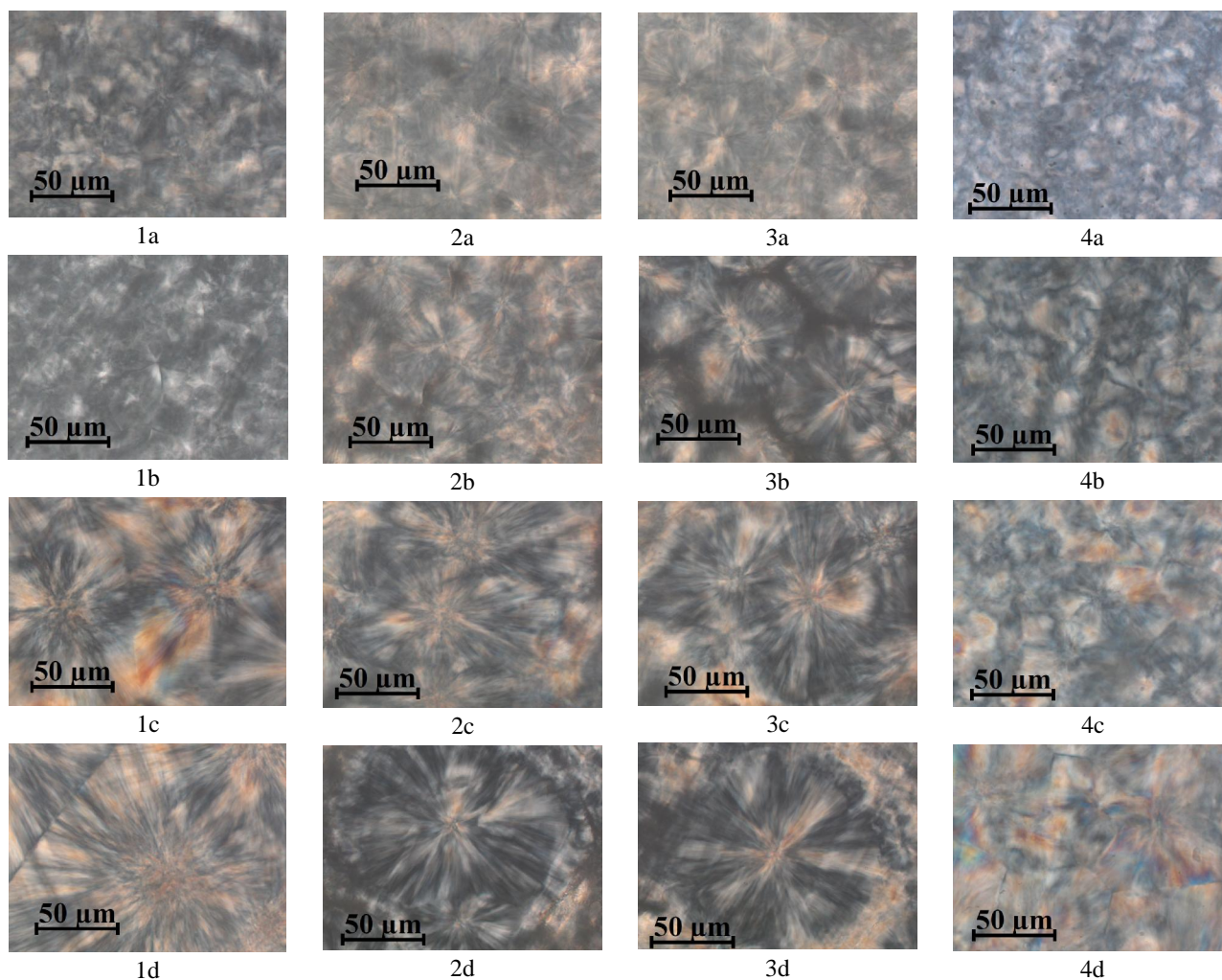

Fig. 2. Microscope photographs of PP (1); mPP (2); bPP (3) and rPP (4) obtained at different crystallization rates (K/min):
64 (a); 16 (b); 4 (c) and 1 (d)

4. Conclusions

　　The melting behavior of four polymers: polypropylene, propylene-based block copolymer, propylene-based random copolymer, and maleic anhydride grafted polypropylene, was studied with DSC and Microscopy. The obtained results indicate that both chemical structure of polypropylene chain and crystallization rate exhibit great influence on the crystalline structure of polypropylene. It was found that the regular introduction of the co-monomer units of any chemical nature (mPP and bPP) and higher crystallization rates lead to the formation of large crystals. On the other hand, structural inhomogeneity of polypropylene chain and increase of crystallization rates promote the formation of polymer finely-grain-like structure.

References

[1] F.Dogan (Ed.): Polypropylene. Intech, Croatia 2012.
[2] Zhu M. and Yang H.: Polypropylene fibers [in:] M. Lewin (Ed.), Handbook of Fiber Chemistry, CRC Press 2007, 139-260.
[3] Papageorgiou G., Achilias D., Bikiaris D. *et al.*: Thermochim Acta, 2005, **427**, 117.
[4] Seki M., Nakano H., Yamauchi S. *et al.*: Macromolecules, 1999, **32**, 3227.
[5] Cai H., Luo X., Ma D. *et al.*: J. Appl. Polym. Sci., 1999, **71**, 93.
[6] Zia Q., Radusch H.-J. and Androsch R.: Microscopy: Science, Technology, Application and Education [in:] A. Mendez-Vilas and J. Diaz (Eds.), Formatex, Badajoz 2010, 1940-1950.
[7] Androsch R., Di Lorenzo M., Schick C. *et al.*: Polymer, 2010, **51**, 4639.
[8] Cho K. and Li F.: Macromolecules, 1998, **31**, 7495.
[9] Holsti-Miettinen R., Seppala J. and Ikkala O.: Polym. Eng. Sci., 1992, **32**, 868.
[10] Nandi S. and Ghosh A.: J. Polym. Res., 2007, **14**, 387.
[11] Jacoby P., Bersted B., Kissel W. *et al.*: J. Polym. Sci., Polym Phys., 1986, **24**, 461.
[12] Lovinger A.: J. Polym. Sci., Polym. Phys., 1983, **21**, 97.
[13] Purez E., Zucchi D., Sacchi M. *et al.*: Polymer, 1999, **40**, 675.
[14] Gou Q., Li H., Yu. Z. *et al.*: Chin. Sci. Bull., 2008, **53**, 1804.
[15] Papageorgious D., Papageorgious G., Bikiaris D. *et al.*: Europ. Polym. J., 2013, **49**, 1577.
[16] Papageorgiou D., Bikiaris D. and Chrissafis K.: Thermochim. Acta, 2012, **543**, 288.
[17] Cho K., Li F. and Choi J.: Polymer, 1999. **40**, 1719.
[18] Salmah H., Ruzaidi C. and Supri A.: J. Phys. Sci., 2009, **20**, 99.
[19] Lukanina Yu., Kolesnikova N., Khvatov A. *et al.*: J. Balk. Tribol. Assoc., 2012, **18**, 142.
[20] Nguen S., Perez C., Desimone M. *et al.*: Int. J. Adhesion and Adhesives, 2013, **46**, 44.
[21] Bershteyn V. and Egorov V.: Differentsialnaya Scaniruyushchaya Calorimetria dlya Fizikokhimii Polymerov. Khimiya, Leningrad 1990.
[22] Ambrogi I.: Polypropylene. Khimiya, Leningrad 1967.

ВПЛИВ ШВИДКОСТІ ОХОЛОДЖЕННЯ В ПРОЦЕСІ КРИСТАЛІЗАЦІЇ НА ТОПЛЕННЯ ПОЛІПРОПІЛЕНІВ РІЗНОЇ ХІМІЧНОЇ БУДОВИ

Анотація. За допомогою диференційної скануючої калориметрії (ДСК) та оптичної мікроскопії досліджено топлення поліпропіленів різної хімічної будови (ізотактичний гомополіпропілен, блок- і статистичні кополімери на основі пропілену і поліпропілену, прищепленого малеїновим ангідридом). Встановлено, що топлення і кристалічна структура поліпропілену та його кополімерів залежать від швидкості кристалізації, хімічної природи комономерних одиниць та регулярності їх розташування в основному ланцюгу поліпропілену.

Ключові слова: поліпропілен, топлення, кристалічна структура, мікроскопія.