

ON THERMAL PROPERTIES OF POLY(4-METHYL-1-PENTENE) MEMBRANES CAST FROM SOLUTION

A. Danch and A. Gadomski

Silesian University, Institute for Technological Problems, Department of Polymer Physics,
41-200 Sosnowiec, Śnieżna 2, Poland

Abstract

Thermoanalytical investigations of poly(4-methyl-1-pentene) membranes of two substantially different types (opaque and transparent), cast from solution, have been carried out using the derivatograph (Q-1500 D). On the basis of simultaneous DTA, TG and DTG measurements, enthalpy changes, weight losses and rates of weight losses have been determined, respectively. DSC has been done using the Perkin-Elmer 7-Series Thermal Analysis System. The results obtained have been used to get some structural information like decompositions and glass as well as crystallization properties of the membrane material.

Keywords: membrane materials, structural properties

Introduction

The problem of how one may conclude on some structural properties of materials having known their basic thermal characteristics is always of interest and, in consequence, leads to many practical implications (new materials, modern technologies, environment protection, etc.). In the situation when a polymer membrane is under consideration, both, the formation of the membrane structure (e.g., whether it is more crystalline than amorphous or oppositely) and physico-chemical conditions assigned to it as well as its main characteristics or feature are recently subjects of careful studies [1]. This is also the case of poly(4-methyl-1-pentene) (PMP) membranes (or films).

PMP is a semicrystalline polymer. Five crystalline modifications were found and the unit-cell structure and dimensions were described in literature [2, 3]. The modification designated mod.I is usually obtained by melt processing of PMP. The other four, mod.II-V, are formed from dilute solutions of PMP in various solvents. However, the modifications or mixtures of modifications can be obtained depending on dissolution temperature, cooling conditions and polymer concentration [4-8].

In this paper, we present thermal (DTA, TG, DTG, DSC) measurements in order to give characteristics of the membranes cast from solution and produced

on the basis of PMP. The purpose of this work is to determine the percent crystallinity of the samples. The effects of including different morphologies on PMP membranes have been examined using DSC-7 (Perkin-Elmer). The influence of thermal history on the position and shape of the glass transition event has been shown. The conditions concerning the formation of the opaque or transparent PMP membranes have been described elsewhere [9].

Experimental

Materials

PMP used in our experiments was originally produced by Mitsui & Co. LTD. and distributed as a TPX-granulate. This granulated PMP product has been used to prepare membranes from several solvents, i.e. carbon tetrachloride (CCl_4), cyclohexane (C_6H_{12}), toluene (C_7H_8), chloroform (CHCl_3), benzene (C_6H_6), chlorobenzene ($\text{C}_6\text{H}_5\text{Cl}$) and trichloroethylene (C_2HCl_3) with no further purification. Two types of films (opaque and transparent) have been obtained under different process conditions mostly depending on temperature regime applied, solvent evaporation rate and polymer concentration in the solution.

Methods

The thermoanalytical investigations have been carried out using the Paulik-Paulik-Erdey derivatograph (Q-1500 D), under the following conditions: atmosphere-air, standard substance- Al_2O_3 , temperature range 20–1000°C, sample size 50–500 mg, heating rate 1.25–20 deg·min⁻¹. The samples have been placed into ceramic crucibles.

The following conditions have been utilized in the DSC analysis of the PMP samples: heating rate – 20 deg·min⁻¹; atmosphere – nitrogen; flow rate – 50 ml·min⁻¹; sample pan-aluminum; reference- empty aluminium pan; sample size-about 10 mg. The measurements have been performed with membranes previously cut into smaller pieces. The same calibration procedures (melting transition of metals, In, Sn, Zn) for both techniques used were done.

Because of importance of PMP concentration in solution on the process of the membrane formation, the membranes were compared, but only at one polymer concentration value chosen (i.e., at 2 wt%). However, solutions of 0.5–4 wt% polymer were prepared and studied as well.

Results and discussion

On the basis of the simultaneous DTA, TG and DTG traces, enthalpy changes, weight losses and rates of weight losses have been determined, respec-

tively, and used for characterization of the decompositions, glass and crystallization process. For all cases, the stability in air atmosphere of TPX-material and membranes-material cast from solutions are almost identical. The beginning of decomposition has been fixed at 215°C (this value changed between 215–235°C, depending on what kind of sample was treated). The decomposition process is represented by a strong exothermic peak which screens an endothermic peak connected to the melting process of PMP crystalline structures. A better separation (and visualization) of those two kinds of peaks can be reached when one ensures a possible small amount of oxygen molecules in the ceramic crucibles (the crucibles can also be filled up by Al_2O_3 and sealed). A very similar effect can be gained when one fills up the device (derivatograph) chamber by a neutral gas (i.e. helium). The melting temperature of PMP obtained from this measurements is about 230°C (it ranges from 220 to 250°C at heating rate $10 \text{ deg}\cdot\text{min}^{-1}$; cf. Fig. 1 for details). Despite of the oxygen absence, after heating up to 600°C the total mass of PMP was absolutely diminished what could lead to the conclusion of degradation and/or destruction of sample under study with presence of some low mass molecular gaseous substances [10].

It is certainly known that several polymers have different modifications (configurations, conformations) which behave in distinctly different manner under thermal treatment. Those modifications, emerged during the polymeriza-

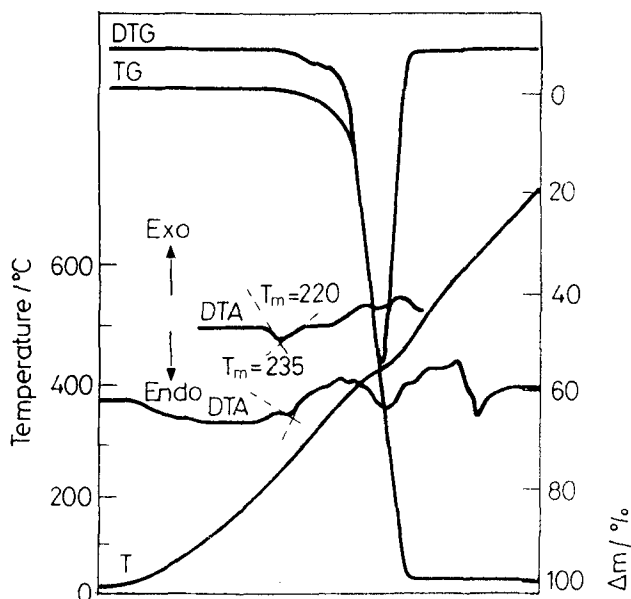


Fig. 1 DTG, TG, DTA curves of TPX in $10 \text{ deg}\cdot\text{min}^{-1}$ of 450 mg samples: 1-lower DTA curve at air atmosphere with sealed crucible, melting point 235°C (225–270°C); 2-upper DTA curve at helium atmosphere, melting point 220°C (215–275°C)

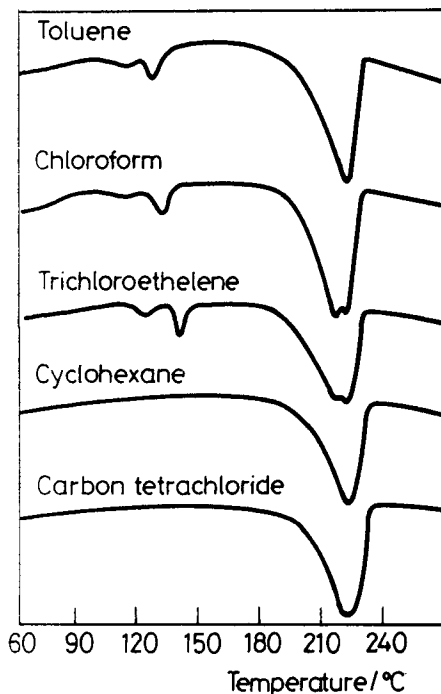


Fig. 2 Melting transition of PMP membranes cast from different solution

tion process and proceeded under different conditions, can differ with respect to the melting temperature [11]. It is possible to transform one crystalline modification to another mostly by either recrystallization from the melt or crystallization from solution at the boiling temperature of solvents applied [12–14]. The existence of those modifications in one sample is possible as well. In this situation two or more transformations in the vicinity of melting temperature point can be observed. For various polyolefines their polymorphic modifications are recognized [12, 15, 16], for which the glass temperatures (T_g) and their melting temperatures (T_m) of crystalline phases were determined. It is also known, that PMP can exist in a certain number of crystalline modifications [5–7]. The detection of those effects, even for highly crystalline polymers, becomes difficult by DTA since its low degree of sensitivity. Therefore, more precisely DSC system was used for observation of glass and crystalline transitions for oriented materials, such as films. The first heat DSC results in the case of five solvent-cast films are depicted in Fig. 2. Some PMP samples have a single melting peak, and the other have more than one melting peak. However, for all solvent-cast PMP films one big melting peak at $225 \pm 2^\circ\text{C}$ has evidence. The existence of other endothermic peaks has been observed earlier for other solvent

and was attributed to modification named in the literature as 'modification I' (it is the usual modification under heating process, i.e. the tetragonal crystal form [8, 17]). The degree of crystallinity was calculated from endotherm area of each trace, taking 61.9 J/g (14.8 cal/g) as the value of heat fusion for the 100% crystalline polymer [17]. The values for investigated membranes are listed in Table 1. Some rough observations are also worthy mention here, namely, in some cases the crystallization process in a gel phase was connected to a whitening of the PMP-mixture. Also, during the cooling from the solvent boiling temperature to the room temperature, the gelation with whitening, but only for cyclohexane, toluene, chlorobenzene and benzene solution with different gelation temperature may occur. The observed ordered forms (like dendrites, spherulites or crystallites) obtained from gel (treated in special way [18]) are similar to that which one can obtain in the numerical experiment using a computer simulations-technique [19] or even analytically, cf. [20, 21] and refs therein.

Table 1 The degree of crystallinity calculated from endotherm area of DSC trace for investigated membrane materials: *-opaque membrane

Casting solvent	Transition energy / J·g ⁻¹	Crystallinity / %
Cyclohexane	20.79	33
	23.48 *	38
Carbon tetrachloride	23.08	37
Toluene	27.72 *	45
Chloroform	30.35	49
Chlorobenzene	24.02 *	39
Trichloroethylene	26.99	44

Semicrystalline polymers were considered to contain two mutually different phases: crystalline and amorphous. Some studies have pointed out that one can divide into constrained and unconstrained domains the amorphous phases [22, 23]. That state caused by biaxial stretching process have a major effect on the morphology of the films and the glass transition as well. Especially, a biaxially oriented thin membranes show differences in DSC results for glass transition. The results obtained for samples are displayed in Fig. 3, and show existence of small endothermic peak in the vicinity of glass temperature for PMP membranes. For thinner (i.e., about 1.5×10^{-5} m) membranes the endothermic peak was more visible. After heating this peak vanished. The same effect was observed after month and T_g values were shifted slightly towards high temperatures. This can be explained by relaxation processes in PMP membranes occurred (especially α relaxation process [9]) for any temperature.

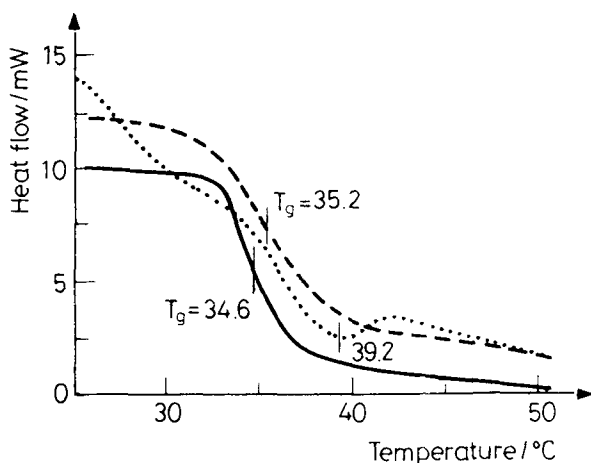


Fig. 3 Comparison of glass transition on PMP membranes with three thermal histories: solid line-sample after shock cooling, dashed line-sample after slow cooling and holding in room temperature for month, dotted line-sample after slow cooling

Conclusions

The opaque PMP membranes possess more porous structure contrary to the other PMP membranes which are transparent. The membranes of both types show similar characteristics concerning their thermostability, glass transition of amorphous phases and degree of crystallinity.

The differences can be seen in various crystalline forms (dendrites, spherulites, etc.) formed during drying process. Especially, it is easy to observe for PMP-benzene gel phase. However, the amorphous biaxially oriented regions have a major effect on the morphology of the thin membranes, what can influence on their permselective properties.

References

- 1 M. Starzak, 'The Physical Chemistry of Membranes', Academic Press, NY, 1984.
- 2 G. Charlet and G. Delmas, *Polymer*, 25 (1984) 1619.
- 3 T. He and S. Porter, *Polymer*, 28 (1987) 1321.
- 4 M. Takayanagi and M. Kawasaki, *J. Macromol. Sci.-Phys.*, (B) 1 (1967) 741.
- 5 S. Aharoni, G. Charlet and G. Delmas, *Macromolecules*, 14 (1981) 1390.
- 6 G. Charlet and G. Delmas, *Polym. Bull.*, 6 (1982) 367.
- 7 G. Charlet, G. Delmas, J. Revol and R. Manley, *Polymer*, 25 (1984) 1613.
- 8 T. Tanigami, H. Suzuki, K. Yamaura and S. Matsuzawa, *Macromolecules*, 18 (1985) 2595.
- 9 A. Danch and K. Jarzabek, 'Far-From-Equilibrium Dynamics of Chemical System'; ed. J. Górecki, A. S. Cukrowski, A. L. Kawczyński, B. Nowakowski, World Scientific, Singapore 1994, pp. 350.

- 10 R. C. Mackenzie, 'Differential Thermal Analysis', Academic Press, London 1970, Vol. 1 Section C and references therein.
- 11 J. P. Kenedy, J. J. Elliot and B. Groten, *Makromol. Chem.*, 77 (1964) 26.
- 12 C. Geacintov, R. B. Miles and H. J. L. Schuurmans, *J. Polymer Sci.*, Part A, 4 (1966) 431.
- 13 C. Geacintov, R. S. Schotland and R. B. Miles, *J. Polymer Sci.*, Part C, 6 (1964) 197.
- 14 D. R. Carter and E. Baer, *J. Appl. Phys.*, 37 (1966) 4060.
- 15 B. H. Clampitt and R. D. Hughes, *J. Polymer Sci.*, Part C 6 (1964) 43.
- 16 B. Ke, *J. Polymer Sci.* 42 (1960) 15.
- 17 J. M. Mohr and D. R. Paul, *Polymer*, 32 (1991) 1236.
- 18 A. Gadomski and A. Danch, unpublished materials.
- 19 A. Gadomski and Z. J. Grzywna, 'Far-From-Equilibrium Dynamics of Chemical System'; ed. J. Popielawski, J. Górecki, World Scientific, Singapore 1991, pp. 417.
- 20 A. Gadomski and J. Łuczka, *Intern. J. Quantum Chemistry*, in press.
- 21 A. Gadomski, Z. J. Grzywna and J. Łuczka, *Chem. Eng. Sci.*, 48(21) (1993) 3713.
- 22 R. J. Seyler and M. Moscato, *Symp. on the Assignment of the Glass Transition*, ASTM E-37, Atlanta, 1993.
- 23 H. A. Hristov and J. M. Shultz, *J. Polymer Sci.*, (Phys.), 28 (1990) 1647.

Zusammenfassung — Unter Anwendung eines Derivatographen Q-1500 D wurden thermoanalytische Untersuchungen von aus Lösung gegossenen Poly-(4-methyl-1-penten)-membranen zwei grundlegend unterschiedlichen Typs (opak und durchsichtig) durchgeführt. Auf der Grundlage simultaner DTA-TG-DTG-Messungen wurden Enthalpieänderungen, Gewichtsverluste und Gewichtsverlustgeschwindigkeiten ermittelt. DSC wurde mit Hilfe eines Thermoanalyse-systemes vom Typ Perkin Elmer Serie 7 durchgeführt. Die erhaltenen Ergebnisse wurden benutzt, um einige Strukturinformationen wie zum Beispiel Zersetzungs-, Glas- als auch Kristallisations-eigenschaften des Membranmaterials zu erhalten.