

MOLECULAR MODELING AND THERMOANALYTICAL STUDIES OF THERMOPHYSICAL PROPERTIES OF SOME POLYMERS

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Abstract

The results of computational modeling and experimental data on some thermophysical properties of selected polymers were compared. Different engineering polymers, e.g. polycarbonates and terephthalate polyesters, were considered and their glass transition temperatures and thermal stabilities were determined, by using thermoanalytical methods, e.g. DSC and TG. Measurements were carried out with Perkin-Elmer DSC 7 and TGA 7 instruments. Molecular modeling and computer calculations were performed at the Interdisciplinary Computer Modeling Center (ICM) of Warsaw University, using a Cray E1 98 computer and the Insight II software of BIOSYM Technologies Inc. Reasonably good agreement was found between the experimental and calculated values of the glass transition temperatures of the investigated polymers, e.g. for poly(butylene terephthalate) T_g (calc.) = 74°C and T_g (experim.) = 70°C. Discrepancies were observed for the temperature of half decomposition $T_{d,1/2}$, some of them can be explained by effects of polymer molecular weight and/or char-forming effects.

Keywords: molecular modeling of polymers, thermal analysis of polymers, temperature of half decomposition

Introduction

Molecular modeling is a very useful tool in polymer science, among others for the prediction of polymer properties, such as miscibility, permeability or mechanical and thermophysical properties.

Molecular simulation methods have been applied to calculate mechanical properties of polymers [1-5]. The structure of aromatic amorphous polysulfone (PSF) and its mechanical and thermal properties were characterized by the molecular simulation technique [6]. The elastic constants and thermal expansion coefficient for PSF was calculated.

Ralston *et al.* [7] used the molecular modeling technique to predict the transport properties of gases in polymers. They studied the sorption and diffusion of carbon dioxide in bisphenol A polycarbonate (PC). The agreement between the calculated and experimental values of the heat of solution ΔH_s for carbon dioxide in PC was found. The calculated values of ΔH_s and the entropy data were then used to predict the gas solubility coefficient.

Recently, comparative studies on various computational techniques used to predict thermal (glass transition) and mechanical (tensile modulus) properties of polyimides were reported [8].

In previous papers [9, 10], molecular modeling results concerning PSF and PC were presented.

In the present work, the results of computational modeling and experimental data obtained by thermoanalytical methods, i.e. differential scanning calorimetry (DSC) and thermogravimetry (TG), were compared for some engineering polymers. The glass transition temperature T_g and the temperature of half decomposition $T_{d,1/2}$ were considered.

Experimental

Materials

The following polymer samples were investigated:

- PC-A - bisphenol A polycarbonate, stabilized pellets of commercial Makrolon LS3100, Bayer AG;
- PC-M - tetramethylbisphenol A polycarbonate, a pilot plant product of ICRI, Warsaw, Poland, in the form of film;
- PC-C - polycarbonate from 1,1-dichloro-2,2-di(4-hydroxyphenyl)ethylene, a laboratory product of ICRI, Warsaw, Poland, in the form of film;
- PBT - poly(butylene terephthalate), commercial polymer Crastin SK 605; Ciba Geigy;
- PET - poly(ethylene terephthalate), an injection molded grade for polymer blends, 'Elana' Chemical Works, Torun, Poland.

Procedures

Molecular modeling

The following methods are commonly used for predicting polymer properties: the classical method of van Krevelen [11], based on group additivity; the Dow method developed by Seitz [12], also based on group additivity; and the Synthia method based on topological information, described by Bicerano [13]. The basic concept of Bicerano's methodology relies on connectivity indices derived from the graph theory and is applicable to any polymer constructed from the following nine elements: C, H, N, O, Si, S, F, Cl and Br. In this work, the Synthia method was applied.

Molecular modeling and computer calculations were performed at the Interdisciplinary Computer Modeling Center at Warsaw University, using a CRAY E1 98 computer and the Insight II/Discover software of Biosym Technologies Inc. (San Diego, CA).

Thermoanalytical measurements

The glass transition temperature (T_g) of polymers was measured by using a Perkin-Elmer DSC 7 differential scanning calorimeter. Measurements were carried out at a heating rate of $20^\circ\text{C min}^{-1}$ in nitrogen atmosphere.

A Perkin-Elmer TGA 7 thermogravimetric analyser was used to study the degradation of polymers in nitrogen atmosphere at a heating rate of 5°C min^{-1} . The values of $T_{d,1/2}$ were determined as a measure of the thermal stability of the investigated polymers [9–11, 13].

Samples of approximately 10 mg were heated from room temperature to 1000°C .

Results and discussion

Model structures of the investigated polymers were constructed, and energy was minimized by the steepest descent and BFGS quasi-Newton iteration techniques. Examples of the modeled structures of PET and PC-M are shown in Figs 1 and 2, respectively.

Experimental and calculated glass transition temperatures of the investigated polymers are given in Table 1.

A reasonably good agreement was found between the experimental and calculated values of T_g for the investigated polymers, except for PC-M and PET.

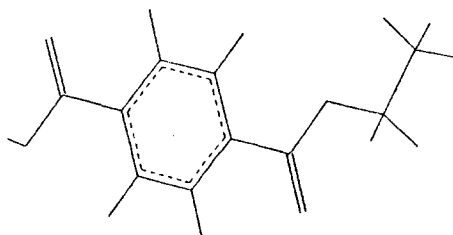


Fig. 1 Model structure of PET

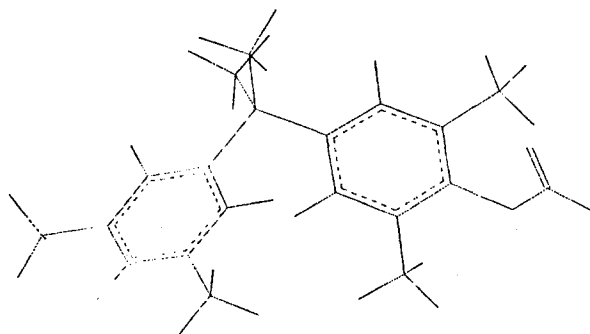


Fig. 2 Model structure of PC-M

Table 1 Glass transition temperatures

Polymer	Experimental	Computer modeling
	$T_g/^\circ\text{C}$	
PC-A	148	143
PC-M	182	196
PC-C	165	167
PBT	70	74
PET	73	97

In the case of PC-M, this may be explained by the effect of molecular weight, since the PC-M sample had a relatively low molecular weight [η]=87 cm³ g⁻¹. According to some literature data [13], T_g for PC-M is 200°C.

In the case of PET, the observed discrepancy cannot yet be explained. However, a similar discrepancy was reported by Bicerano [13]: T_g =77°C experimentally, and T_g =100°C from calculations.

The results of thermogravimetric and molecular modeling calculations are given in Table 2.

Table 2 Temperature of half decomposition, $T_{d,1/2}$

Polymer	Experimental	Computer modeling
	$T_{d,1/2}/^\circ\text{C}$	
PC-A	478	398
PC-M	523	452
PC-C	610	426
PBT	425	452
PET	457	459

Computer modeling calculations confirmed that the thermal stabilities of the polycarbonates follow the sequence PC-A < PC-C < PC-M. This is in agreement with our earlier thermogravimetric findings on the decomposition of PC in air, where the apparent activation energies of decomposition of PC in air, E_a , calculated according to Kissinger's method, exhibit the same sequence [14]. However, it should be noted that the values of E_a depend on the conversion degree, and the sequence of E_a for low conversion degree is PC-C < PC-A < PC-M.

The experimental values of $T_{d,1/2}$ for PC are higher than the calculated ones, and a particularly high value of experimental $T_{d,1/2}$ was observed for PC-C. This may be explained by the char-forming effects, where halogen atoms are considered as soot formers engaged in secondary reactions [11], changing the mechanism of polymer decomposition.

For the terephthalate polyesters, agreement between the experimental and computer modeling values of $T_{d,1/2}$ was observed.

Concluding remarks

A reasonably good agreement was found between the experimental and calculated values of the glass transition temperature T_g for the investigated polymers.

Some discrepancies were observed for the temperature of half decomposition $T_{d,1/2}$ for PC. In the case of PC-C, char-forming effects seem to be responsible for the observed discrepancy in $T_{d,1/2}$.

The Synthia method can be considered as a convenient tool for investigations of physicochemical properties of polymers, in particular for screening the thermal stability of polymer materials.

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Polymer modeling computations were performed at the Interdisciplinary Computer Modeling Center (ICM) of the Warsaw University, where a CRAY EL 98 computer and the software of BIOSYM Technologies, Inc. were used.

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