

THERMAL ANALYSIS OF LADDER POLYMERS OBTAINED FROM MULTIMONOMERS

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Abstract

Differential scanning calorimetry and thermogravimetry were used to examine the thermal behaviour of the multimonomers poly(2-methacryloyloxyethyl methacrylate) and poly(2-acryloyloxyethyl methacrylate), of the ladder polymers prepared by the template polymerization of these multimonomers, and of a linear analogue of the ladder polymers, poly(2-butyrylethyl methacrylate). The results obtained show that only one of the ladder polymers has a considerably higher thermal stability than that of their linear analogue.

Keywords: ladder polymer, multimonomer, thermal analysis, thermal stability

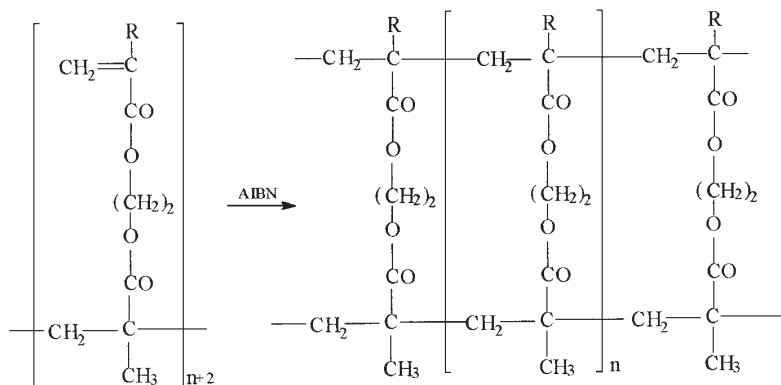
Introduction

It has been postulated that polymers would achieve greater thermal stability if they possessed a 'ladder' structure. The reasoning behind this is that two bonds must then be broken instead of one in order to sever the polymer chain. Theoretical calculations have been made by Tessler [1] on hypothetical structures of ladder type. It was assumed that each bond was of equal stability and that scission occurred entirely at random at an arbitrary rate. Mass losses and changes in molecular mass were computed and compared with those for an analogous linear polymer. The results demonstrated the improvement in stability, based on the loss in mass of a ladder polymer as compared with one with a single chain structure.

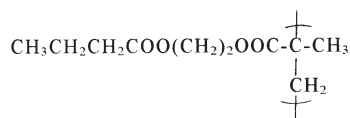
In the literature, however, there is a dearth of adequate experimental verification of such theoretical treatment to show that ladder polymers have higher thermostability than their linear analogues. The high thermostability of a ladder polymer is conditioned by the low probability of formation of volatile decomposition products when the bonds in a macrochain are broken, and by an increase in the probability of recombination of broken bonds at the expense of a cell effects [2, 3].

The present paper reports our findings concerning the thermal stabilities of the multimonomers poly(2-methacryloyloxyethyl methacrylate) and poly(2-acryloyloxyethyl methacrylate) and of the ladder polymers prepared by the template polymeriza-

tion of these multimonomers (Scheme 1), in comparison with the thermostability of a linear analogue of the ladder polymers in the form of poly(2-butyrylethyl methacrylate) (Scheme II):



where $R=H$ or CH_3



Experimental

Materials

The multimonomers poly(2-methacryloyloxyethyl methacrylate) (MM) and poly(2-acryloxyethyl methacrylate) (MA) were prepared by Schotten-Bauman esterification of poly(2-hydroxyethyl methacrylate) with methacryloyl or acryloyl chloride, according to the procedure described previously [4–6]. MM has $M_n=21300$ and $M_w/M_n=2.2$, while MA has $M_n=22900$ and $M_w/M_n=2.4$.

2-Butyrylethyl methacrylate was prepared by esterification of 2-hydroxyethyl methacrylate with butyric anhydride, using perchloric acid as catalyst [7].

The ladder-type polymers were prepared by free-radical polymerization of MA and of MM according to the template mechanism, under selected reaction conditions, i.e. with $[MM] \approx [MA] = 6.51 \cdot 10^{-2} \text{ mol dm}^{-3}$ and $[AIBN] = [1.46 \cdot 10^{-3} \text{ mol dm}^{-3}]$, at 75°C , in dioxane as solvent [6, 8]. The ladder polymer (PMM) prepared by the polymerization of MM has $M_n=25700$ and $M_w/M_n=2.5$, while the ladder polymer (PMA) prepared from MA has $M_n=24600$ and $M_w/M_n=2.6$.

Poly(2-butyrylethyl methacrylate) (PBM) was prepared by polymerization of a 10% solution of the monomer in dioxane. The concentration of AIBN was 2% by mass in rela-

tion to the monomer. The reaction temperature was 70°C. The polymer was recovered by precipitation in hexane and purified by reprecipitation, using dioxane/hexane. The polymer obtained has $M_n=34300$.

Methods

Infrared spectra were recorded with a Perkin Elmer 2000 Fourier transform infrared instrument.

Chromatograms were run on a Hewlett-Packard HP-1050 instrument in a PLgel 5 μm Mixed-C column at 80°C, at an eluent flow rate of 0.8 $\text{cm}^3 \text{min}^{-1}$. An RI detector HP 1047A was used. The average molecular mass was calculated from a polystyrene standard calibration curve.

Differential scanning calorimetry (DSC) of multimonomers, ladder polymers and their linear analogue was performed with a Perkin Elmer, DSC-7 instrument. The conditions of the experiments were as follows: heating rate 10°C min^{-1} , rate of nitrogen flow 30 $\text{cm}^3 \text{min}^{-1}$, mass of sample 5–10 mg. The samples were placed in an aluminium pan, and an aluminium cover was crimped on.

Thermogravimetric analyses were performed with a Hungarian derivatograph (Paulik, Paulik and Erdey system). The conditions of analysis were as follows: medium, air; platinum plate; standard substance Al_2O_3 ; temperature range 25–800°C, sample size 60 mg; heating rate 7.9°C min^{-1} . Sensitivity: DTA 1/5; DTG 1/20; TG 100, as determined in [9]. The temperature of beginning of mass loss, the temperature of 10% mass loss T_{10} , the temperature of 50% mass loss T_{50} , and the residue after heating to 800°C were determined from the TG curves. Prior to thermal analysis, the samples were dried in a vacuum dryer at 50°C for 24 h.

Results and discussion

The free-radical polymerization of MM and MA has been studied previously [6, 8]. It was found that MM and MA polymerize according to the template mechanism (along ordered acryl and methacryl units on the polymeric chain) under the selected reaction conditions. Such a course of reaction is confirmed by the fact that the molecular masses and the molecular mass distribution of the analyzed products hardly change with the extent of conversion. The polymerization products formed under such reaction conditions have ladder-type structures.

The IR spectra of the multimonomers (MM and MA) and the ladder polymers (PMM and PMA) are presented in Figs 1 a–d. In comparison with the IR spectra of the multimonomers, the IR spectra of the resultant polymers display almost no absorption band due to double bonds at 1635 cm^{-1} , which confirms that virtually all these bonds have participated in the polymerization process.

DSC curves of MM and MA are depicted in Figs 2 a–d. In the first cycle of heating in the DSC, exothermic peaks can be observed, with maximum at 145 for MM and at 139°C for MA (Figs 2a, b). These exotherms probably result from the thermal polymerization of the double bonds of the multimonomers, leading to cross-linked

products, which is confirmed by the disappearance of the absorption bands of the double bonds in the IR spectra ($\nu=1635\text{ cm}^{-1}$) of MM and MA after heating to 195°C , and by the courses of the curves of MM and MA samples during the second cycle of

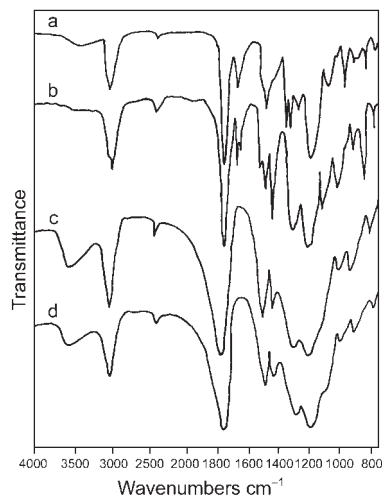


Fig. 1 Spectra FTIR of a – poly(2-methacryloyloxyethyl methacrylate);
b – poly(2-acryloyloxyethyl methacrylate);
c – ladder polymer obtained with poly(2-methacryloyloxyethyl methacrylate);
d – ladder polymer obtained with poly(2-acryloyloxyethyl methacrylate)

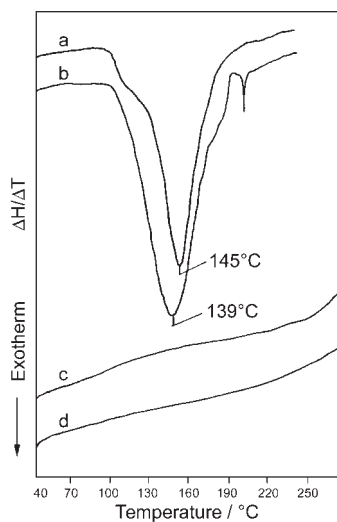


Fig. 2 DSC curves of a – poly(2-methacryloyloxyethyl methacrylate) 1st heating;
b – poly(2-acryloyloxyethyl methacrylate) 1st heating;
c – poly(2-methacryloyloxyethyl methacrylate) 2nd heating;
d – poly(2-acryloyloxyethyl methacrylate) 2nd heating

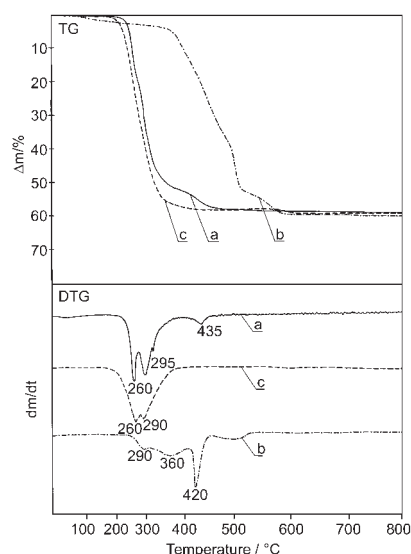


Fig. 3 TG curves of a – ladder polymer obtained with poly(2-methacryloyloxyethyl methacrylate); b – ladder polymer obtained with poly(2-acryloyloxyethyl methacrylate); c – poly(2-butyrylethyl methacrylate)

heating (Fig. 2c,d). Within the examined temperature range, only an increase in $\Delta H/\Delta T$ with temperature is observed for these samples. Similar results were obtained by Vera-Graziano *et al.* [10] for poly(dimethylsiloxane) with various degrees of cross-linking. Moreover, the cross-linking of the multimonomers on heating was confirmed by the fact that they became insoluble in organic solvents.

The DSC curves of the ladder polymers PMM and PMA indicated no phase transitions within the examined temperature range from 40 to 270°C. On the other hand, within the temperature range from –40 to 200°C, the DSC curve of the linear analogue of the ladder polymers, PBM, revealed the glass transition temperature $T_g = -18^\circ\text{C}$.

Figure 3 a–c shows the TG curves of the ladder polymers and their linear analogue. Table 1 contains the results of the derivatographic analyses of these polymers. The temperature of the beginning of mass loss was determined by using not only the TG curves, but also the DTG curves.

Table 1 Results of thermal analysis of PMM, PMA and PBM

Sample	Temperature of onset of mass loss/ $^\circ\text{C}$	Temperature/ $^\circ\text{C}$ of		Mass loss at 800 $^\circ\text{C}/\%$
		10% mass loss/ T_{10}	50% mass loss/ T_{50}	
PMM	230	250	300	2.5
PMA	270	280	460	0
PBM	200	230	270	2.5

It follows from the TG and DTG curves of all the examined samples that a slight and gradual loss in mass is initially observed, which can result from the evaporation of

residual water and volatile impurities. The thermal decomposition of the ladder polymers begins at about 230 for PMM and about 270°C for PMA, and takes place within quite a wide range of temperature, especially in the case of PMA. The temperature of initial decomposition of the analogue of the ladder polymers (PBM) is lower, at about 200°C, while its thermal decomposition proceeds within a narrow temperature range. The unexpectedly slight difference in thermal stability of the ladder polymer PMM and its linear analogue PBM is probably connected with defects in the PMM structure.

The higher thermal stability of the ladder polymers in comparison with that of their linear analogue seems to be associated with a low probability of formation of volatile decomposition products in the case of the ladder structures, and with a higher probability of recombination of the broken bonds in the multimember ring (a cage effect). The results obtained confirm the theoretical considerations of Tessler [1] for this type of ladder polymers.

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