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THERMAL STUDY OF IRRADIATED POLYACETYLENE FILMS

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Abstract

Polyacetylene films irradiated by γ-rays up to 100 MRad were studied by means of TMA, DTG and DSC methods.

It is shown that as the irradiation dose increases the concentration of topological branching knots into the polymer chains and the T_g values decrease, the total mass loss and the enthalpy of the thermal isomerization reaction also decrease.

Keywords: DSC, DTG, polyacetylene films, TMA

Introduction

Although polyacetylene (PA) is the most extensively studied conductive polymer, it is an infusible, insoluble material, unstable in air and it has poor mechanical properties. In order to modify these characteristics, some research groups have studied more stable PA forms or new synthetic routes to obtain PA films with improved mechanical and electrical properties [1–5].

In the thermal analysis of *cis*-PA by differential scanning calorimetry (DSC), three peaks have been observed in the vicinity of 145, 325 and 430°C [6]. The first exothermic peak at 145°C was attributed to the *cis–trans* isomerisation on the basis of infrared (IR) spectra. Another exothermic peak at 325°C was assigned to crosslinking reactions with hydrogen migration. The broad endothermic peak near 430°C is due to thermal decomposition. The mechanism of the *cis–trans* isomerization of PA has been discussed on the basis of IR spectra [6, 7]. Structural changes and kinetic analysis during *cis–trans* isomerization have also been discussed [8, 9].

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Experimental

Polyacetylene films were prepared by the standard Shirakawa technique by polymerization of acetylene on the surface of the catalyst solution $Ti(OC_4H_9)_4$–$Al(C_2H_5)_3$, as described previously [5]. The irradiation was carried out by exposing the samples to ^{60}Co gamma rays up to a dose of 10–30 MRad, or by electron beam (3,5 MeV) from the linear electron accelerator U-12 made in Russia, with three different doses of 50, 70 and 100 MRad (5 mA·cm^{-2}; 5, 10 and 15 min respectively). The films were placed in vials, which were then evacuated, filled with Ar and cooled down with liquid nitrogen vapours to prevent overheating upon electron beam irradiation.

Thermomechanical investigations were carried out with a thermal alyser UIP-70-M made in Russia, at a heating rate of 2.5 deg·min^{-1}, and a loading of 200 mg.

DSC was carried out over the temperature range 70–450°C, with a DSM-2M instrument made in Russia. The DSC instrument was calibrated following the standard procedures. Phase transitions were studied at a heating rate of 16 deg·min^{-1}. Typical sample weights were 6–9 mg. The experiments were carried out under dry nitrogen or air atmosphere.

The TG experiments were done with a Derivatograph-C (Hungary) under identical conditions of heating rate 5 deg·min^{-1}, sample mass 45 mg, and in an air atmosphere.

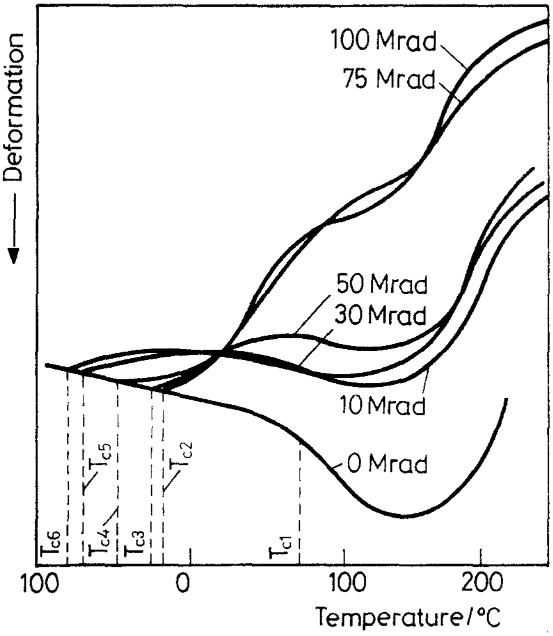

Fig. 1 TMA curves of PA

Results and discussion

Thermomechanical analysis

Figure 1 shows thermomechanical curves of irradiated and non-irradiated PA samples. The non-irradiated PA is seen to have a thermomechanical slope of the curve (TMC) typical of a linear polymer, on which a linear expansion section in the glass state turns (through glass transition) into a curve of high-elastic expansion, the latter turning to an exponential deformation of an established flow process.

From the TMA data, on the basis of a specially developed technique [10], such PA characteristics as M_w, M_n were determined. The curves of molecular

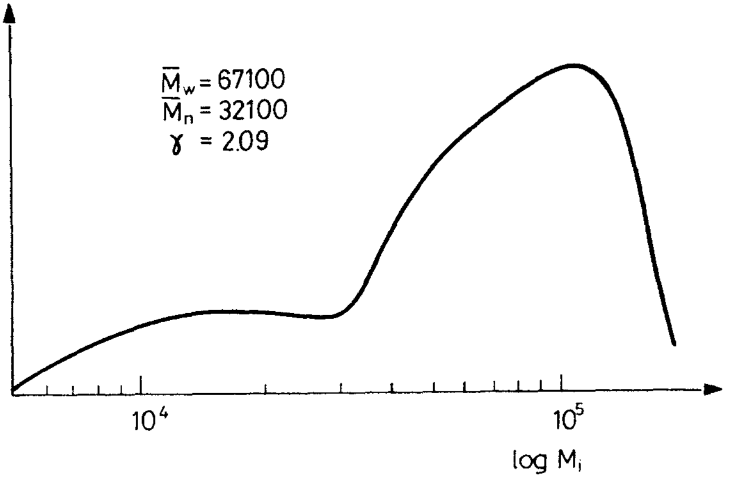

Fig. 2 MWD of PA

Table 1 Dependence of the concentration of topological knots θ_T, crosslinks θ_x, total concentration of interknot chains θ_s, the temperature of attaining the high elasticity plateau T_∞, on the irradiation dose, based on TMA data

Irradiation dose/	Concentration / mol·cm^{-3}×10^{-4}			T_∞ /
MRad	θ_T	θ_x	θ_s	°C
0	0.0	0.0	0.0	–
10	0.0753	0.0005	0.076	350
30	0.116	0.0050	0.121	216
50	1.375	0.0050	1.380	214
70	1.959	0.0110	1.960	217
100	0.908	0.0025	0.908	300

weight distribution (Fig. 2) and content-ration of topological knots of chain interlacing and chemical crosslinks were calculated. All data are given in Table 1.

Polymers 2–6 irradiated with different doses have TMC characteristics of a partially crosslinked polymer with topological branching knots predominating in the gross network. The appearance of branching knots confuses interchain interaction, which leads to a decrease in the glass transition temperature as well. This series of polymers (1–6) shows an explicit exponential character of the glass transition temperature (T_g) *vs.* irradiation dose curve (Fig. 3).

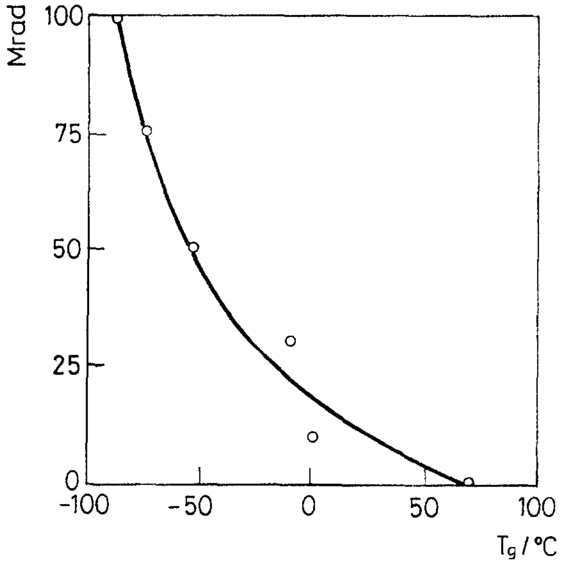

Fig. 3 The influence of the irradiation dose on the T_g of PA

Derivative thermogravimetric analysis

DTG results (Table 2) show that irradiation of PA decreases the temperatures of:

- the maximum sample mass gain due to oxigen addition;
- the beginning of mass loss;
- 10% of the mass loss;
- the total mass loss at 500°C, i.e. the irradiated sample loses mass to a smaller degree (a few per cent).

In Fig. 4 are plotted the characteristic curves of mass loss (TC) for PA irradiated with doses of 10 and 100 MRad, respectively.

It should be noted that for the PA stored in air (Fig. 2) and for TG experiments in an air atmosphere not marked effect of irradiation was detected (oxidation reaction).

Table 2 Dependence of change in mass and temperature for PA on the irradiation dose, based on DTG data

Irradiation dose/ MRad	Weight gain PA / %	Temperature / °C Maximum weight gain	Temperature / °C Beginning of weight loss	Temperature / °C 10% of weight loss	Weight loss at 500°C/ %
0	7.4	254.6	348.0	408.6	31.4
10	9.3	252.0	346.8	407.6	31.0
30	8.0	250.8	345.8	407.6	29.7
50	7.7	245.0	342.0	405.2	29.6
75	7.2	241.3	341.0	405.0	29.3
100	8.3	239.0	339.4	401.7	27.6

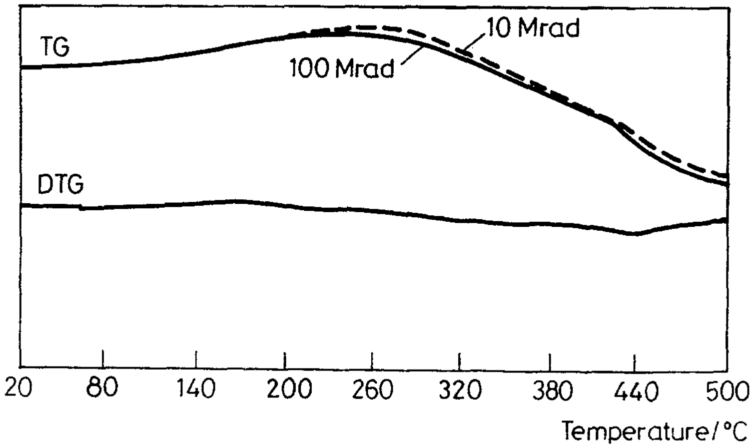

Fig. 4 TG and DTG heating curves of PA

We have determined kinetic characteristics of the thermal decomposition of PA for the temperature range 410–500°C: the activation energy is 260±10 kJ·mol^{-1} and the reaction order is 2 (for non-irradiated PA), while for all the irradiated PA samples the activation energy is, on the average, 220±20 kJ·mol^{-1} and the reaction order is about 1.5.

Differential scanning calorimetry

Figure 5 shows DSC curves recorded for polyethylenes in an inert atmosphere (a) and in air (b). It is apparent from these figures and Table 3 that there are certain differences in the thermal behaviour of irradiated and non-irradiated PA samples.

With increasing irradiation dose, the onset of the *cis-trans* izomerization of PA in an inert atmosphere is shifted to higher temperatures. A somewhat higher

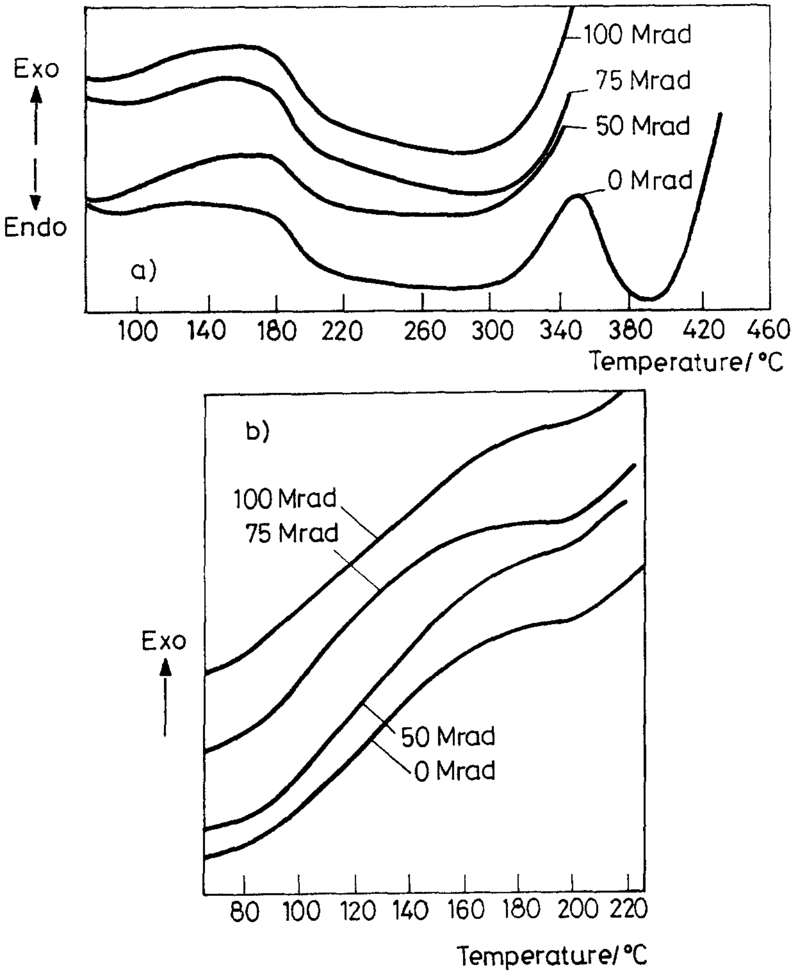

Fig. 5 DSC curves of PA in argon (a) and in air (b)

temperature of the onset of the isomerization reaction (110°C) taken from the literature [6] is explained by a high heating rate (60 deg·min^{-1}), while in our work it was 16 deg·min^{-1}. Here the enthalpy of the isomerization reaction is lowered from 28.2 cal/g (for non-irradiated PA) to 22.1 cal/g (for PA irradiated with a dose of 100 Mrad), which is accounted for by formation of chemical cross-links impeding the isomerization. It seems likely that chemical crosslinks are formed during prolonged storage of PA samples in air. An indirect evidence of this fact is provided by the data in Table 3 for PA samples stored in air in closed aluminium cups. It is the formation of chemical bonds between the polymeric chains that leads to a sharp drop in the glass transition temperature from +70°C (for non-irradiated PA) to −85° (for PA irradiated with a dose of 100 MRad).

Table 3 The temperatures of onset and end of heat release, enthalpy of isomerization of *cis–trans* PA depending on the irradiation dose based on DSC

Irradiation dose/	Heat release temperature/ °C		ΔH /
MRad	onset	end	cal·g^{-1}
0	82/94	206/197	28.2
	– /113*	– /223*	25.2
	110/ –**	165/ –**	
50	84/94	212/198	–
75	90/93	214/200	26.3
	– /114*	– /206*	20.5
100	92/86	218/202	22.1

Note: Numerator – in argon;
Denominator – in air
* – after storage in air for 2 months in the measuring cup;
** – data from the literature [6]

Conclusion

The results of studies on irradiated polyacetylene clearly demonstrate the usefulness of TMA, TG and DSC methods for the characterization of polymeric materials. Valuable information such as $\overline{M}_w$, $\overline{M}_n$, glass transition temperature, enthalpy, etc., which can help in the optimization of material selection and quality control can be quickly and easily obtained. If the TMA technique is coupled with other thermal analysis methods such as thermogravimetry and differential scanning calorimetry, an even more complete evaluation of material properties of such interesting polymers as polyacetylene can be made.

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