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THE THERMAL DEGRADATION OF POLY-(DIMETHYL ITACONATE-co-4-VINYLPYRIDINE)

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Abstract

Copolymers of dimethyl itaconate (DMI) and 4-vinylpyridine (4VP) were synthetized in toluene at 60°C with 0.26 mol% of AIBN as initiator. Their compositions were determined by differential refractometry and by differential scanning calorimetry. The 4VP contents of the copolymer samples ranged between 7 and 75 mol%. The reactivity ratios calculated via the Fineman-Ross method were r_1=0.24 (DMI) and r_2=0.57 (4VP).

The thermal degradations of these copolymers were studied. The results of thermogravimetric measurements indicated that the copolymers degrade at lower temperatures than those of their parent homopolymers. A possible explanation of this anomalous behaviour is the formation of thermally unstable structures during the copolymerisation.

Keywords: copolymers, differential scanning calorimetry, thermal stability, thermogravimetry

Introduction

Polymer science has undergone great development in the past few decades. During this period, many new polymers have been synthesized, with a great variety of different chemical structures and properties. It has become evident that the synthesis of new polymers is not necessarily a prerequisite for the production of materials with new performances. The copolymerisation of existing monomers has been found to be an effective technique for the modification of polymer properties and the production of new materials. Better thermoplastic and elastomeric materials can also be produced by blending polymers, thereby achieving a wider field of application.

Copolymers and blends can undergo complex thermal degradation, and the investigation of such processes is of great practical interest.

The presence of a comonomer may either stabilize or destabilize the copolymer in comparison with the parent homopolymers. An example of the former case is the copolymer of methyl methacrylate with styrene, which has higher thermal stability than that of poly(methyl methacrylate), even at low styrene concentrations. This stabilizing effect is connected with the fact that the presence of styrene in the polymeris-

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ing mixture significantly modifies the mechanism of polymerisation, giving rise to a termination reaction exclusively between unlike radicals. The resulting copolymer contains only a small fraction of unsaturated chain ends through which degradation is initiated [1]. Other statistical copolymers have also been investigated [2–4].

In this paper, we report a study of dimethyl itaconate (DMI)/4-vinylpyridine (4VP) statistical copolymers, covering a wide composition range, the main interest relating to the effect of the introduction of 4VP units into the PDMI molecule.

Experimental

Monomers: 4VP (Merck, p.a.) was distilled before use, and DMI (Fluka, p.a.) was re-crystallized from methanol.

Homopolymer P4VP and copolymer PDMI-co-4VP samples were prepared by solution polymerisation in toluene at 60°C, with AIBN as initiator, while PDMI was synthesized in bulk at the same temperature. The degree of conversion was kept under 15%. The copolymers were purified by repeated precipitation in petroleum ether from toluene solution, and dried to constant mass under vacuum at room temperature.

The copolymer composition was determined by measuring the specific refractive index increments in THF with a Brice Phoenix-2000 differential refractometer.

The T_g values for all samples were determined by using a Perkin Elmer DSC-2 thermoanalyser at a heating rate of 20 K min^{-1}. Each sample was subjected to several heating/cooling cycles to obtain reproducible T_g values.

The thermal behaviour of all samples was determined with a TGS-2 Perkin Elmer instrument. Non-isothermal experiments were performed in the temperature range 30–600°C at heating rates of 2.5, 10, 20 and 40 K min^{-1}, with samples of approximately 5 mg and a N_2 flow rate of 25 cm^3 min^{-1}.

Results and discussion

Copolymer composition data, together with T_g and dn/dc values, are presented in Table 1. A linear relationship was established for the dependence of T_g values on composition.

The limiting viscosity numbers for all copolymer samples, determined in THF at 25°C, were between 16 and 22 cm^3 g^{-1}.

The copolymerisation constants at 60°C were calculated from the composition data by the Finneman–Ross method [5] to be r_1=0.24 (DMI) and r_2=0.57 (4VP).

The thermal degradation of the polymers investigated may induce many different degradation reactions; it is useful to divide these into two classes, main-chain scission and substituent reactions. Main-chain scission includes depolymerization, random degradation, etc. For example, it has been established, e.g. by thermal volatilisation analysis [6], that PMMA thermally decomposes by depolymerization. Substituent reactions take place in the substituents on the polymer backbone, and the chemical structure of the repeat unit is changed, sometimes leaving the main chain intact. Volatile products in this case, if there are any, will not contain monomers.

Table 1 Refractive index increments in THF and T_g values for PDMI, P4VP and PDMI-co-4VP samples

Polymer	d*n*/d*c*/cm^3 g^{-1} in THF	T_g/K	4VP content/mol%
PDMI	0.093	368.0	0
Copolymer 1 (K-1)	0.105	376.0	7
Copolymer 3 (K-3)	0.117	393.7	32
Copolymer 4 (K-4)	0.145	414.0	63
Copolymer 5 (K-5)	0.159	419.0	75
P4VP	0.195	429.0	100

The thermal behaviour of all samples was investigated by means of thermogravimetry (TG). TG curves for PDMI, P4VP and copolymers, obtained at a heating rate of 2.5 K min^{-1}, are presented in Fig. 1. The best separation of the reaction peaks was obtained at a low heating rate.

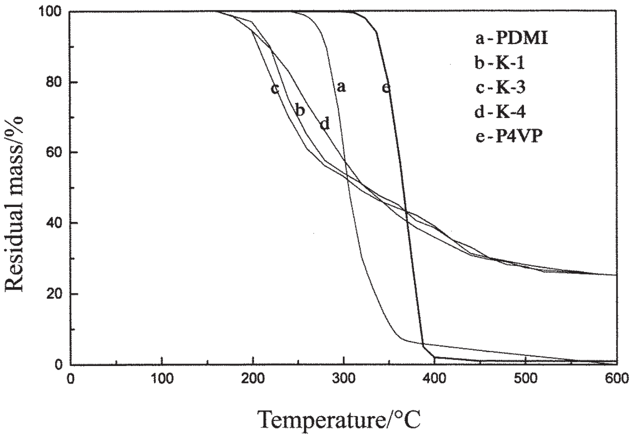

Fig. 1 TG curves of a – PDMI; b – K-1; c – K-3; d – K-4 and e – P4VP; heating rate: 2.5 K min^{-1}

Comparison of the samples is easier by analysing the differential thermogravimetric (DTG) curves presented in Fig. 2, which better reveal the complexity of the process. The peak maxima of these curves represent the maximum decomposition rate at the given temperature, during the degradation of thermally weak structures. As regards the behaviour of the homopolymers, it is evident that P4VP is thermally more stable than PDMI and degrades in a one-step process, with the peak maximum at 405°C.

PDMI is structurally similar to PMMA, and the volatile products of its thermal degradation contain approximately 90% monomer, together with volatile compounds resulting from the scission of the substituents [7]. The similarity in their thermal behaviour is to be expected from the fact that their DTG curves display maxima at simi-

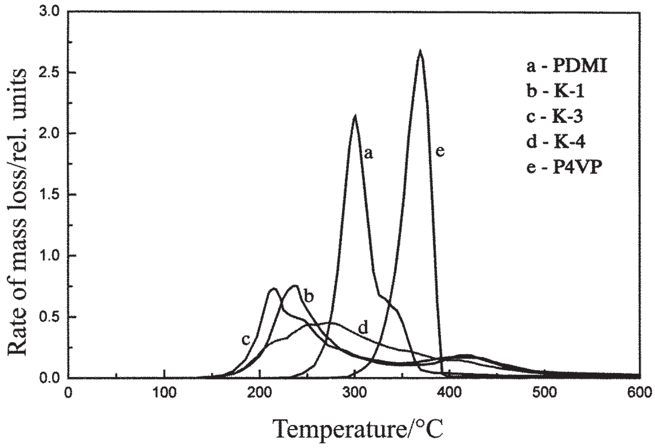

Fig. 2 DTG curves of a – PDMI; b – K-1; c – K-3; d – K-4 and e – P4VP; heating rate: 2.5 K min^{-1}

lar temperatures, although the DTG peak originating from chain-end unsaturated depolymerization is much larger for PDMI.

The polymerisation and non-oxidative thermal degradation of PMMA produced by a free radical process have been investigated in detail [8–11]. It was concluded that the three DTG maxima observed are due to depolymerization initiated by the scission of head-to-head bonds, the scission of bonds in the β position to chain-end unsaturation, and main-chain scission.

The DTG curve for PDMI has one peak with a shoulder, the degradation starting at ca 230°C. The peak is connected with the depolymerization initiated by the chain end unsaturated polymer molecules and the shoulder to depolymerization initiated by the main-chain scission. The peak due to the scission of head-to-head bonds is not detectable in the DTG curve for PDMI [7].

The P4VP homopolymer exhibits one degradation step, starting at ~320°C, with a mass loss of 98% at 600°C.

The DTG curves for the copolymers reveal a complex degradation process under non-oxidative conditions, and the shapes of the curves change with the copolymer composition. One common conclusion for copolymers K-1, K-3 and K-4 is that the degradation starts at a lower temperature (around 175°C) than for either homopolymer. It is evident that the introduction of 4VP units into PDMI furnishes thermally less stable chain structures. The DTG maxima of the polymers obtained at a heating rate of 2.5 K min^{-1} are presented in Table 2.

The copolymer with the PDMI content of 37%, K-4, reveals the most complicated degradation process, with four (five) maxima and it is not possible to provide an explanation without additional analyses.

The degradation processes in copolymers with higher PDMI contents, K-1 (93%) and K-3 (68%), are less complicated and will be discussed in more detail.

Table 2 DTG maxima of polymers obtained at a heating rate of 2.5 K min^{-1}

Polymer	T_{max1}/K	T_{max2}/K	T_{max3}/K	T_{max4}/K	T_{max5}/K
PDMI	300	352 (sh)	–	–	–
K-1	239	414	–	–	–
K-3	218	244 (sh)	–	420	–
K-4	210 (sh)	257	280	370 (sh)	410 (sh)
P4VP	373	–	–	–	–

sh – shoulder

The DTG curves for copolymers K-1 and K-3 (Fig. 2) reveal that there are two decomposition regions. The first starts at ca 160°C and is probably due to the degradation of PDMI, but the peak maximum is situated at lower temperatures as compared with PDMI. The second decomposition region starts at temperatures higher than 300°C and is due to the charring process. The lower temperature peak for K-3 has a shoulder, as in the case of pure PDMI, but such a shoulder is not present in the case of K-1. The first peak for PDMI is ascribed to the depolymerization of chain-end unsaturated polymer molecules, and the shoulder to the main-chain scission initiation of depolymerization; the lack of a shoulder for K-1 might be due to some different source of degradation of the unstable polymer structures. The lower temperature degradation may be initiated by weak links, e.g. head-to-head linkages and end-group unsaturation, while at higher temperatures primary degradation is a random scission process.

The degradation of the pure homopolymers results in a very small residue (P4VP) or no residue (PDMI) at 600°C, but the degradation of the copolymers (K-1, K-3 and K-4) furnishes more residue than expected (approximately 25 mass%), indicating that DMI is also incorporated into the residue. Poly(vinylpyridines) seem to have a catalytic effect on the decomposition of PDMI. This can be explained by the fact that the pyridine ring is a well-known catalyst for the hydrolysis of esters, with the nitrogen atom in the pyridine ring as the main reactive point. The residue is the same for all copolymers, and it can therefore be assumed that the pyridine ring exhibits high catalytic activity, even at low concentration.

The carboxyl groups formed during hydrolysis associate with the 4VP residue in the polymer-polymer complexes via strong specific interactions due to hydrogen-bonds, which leads to physical cross-linking of the material at higher temperatures [12]. For this reason, high amounts of residue remain at 600°C for all these copolymers.

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