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Fullerene C_{60} as stabiliser for acrylic polymers

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Abstract

The influence of fullerene C_{60} additives on thermal behaviour and thermodegradation of poly-*n*-alkyl acrylates, from butyl to heptyl, and of corresponding polymethacrylates was investigated by thermogravimetry in dynamical conditions and pyrolysis/gas chromatography in isothermal conditions at 400–650 °C. The fullerene is a well-known efficient acceptor of radicals and its presence influences the thermal degradation of acrylic polymers, shifting the decomposition process from a radical pathway to a non-radical mechanism. For poly-*n*-alkyl acrylates the addition of fullerene leads to increase in the yields of olefin and alcohol, degradation products coming from non-radical pathways. On the other hand, the yields of the pyrolysis products deriving from the random main-chain scission, i.e. monomer, dimer, saturated diester, trimer, corresponding acetate and methacrylate, decrease. The recorded temperatures of maximum weight loss (obtained by thermogravimetric experiments) are slightly increased by the presence of fullerene. The effect of fullerene is more noticeable in the thermal behaviour of poly-*n*-alkyl methacrylates, in fact the enhancements of the temperature of maximum weight loss are 19–25 °C. The mixtures containing fullerene give rise to a marked decrease of the monomer yield and, at the same time, an increase of olefin and methacrylic acid amounts. The fullerene acts as radical acceptor suppressing the unzipping process and favouring the non-radical side-chain reactions.

Keywords: Poly-*n*-alkyl acrylates; Poly-*n*-alkyl methacrylates; Fullerene C_{60}; Stabiliser; Pyrolysis–gas chromatography; Thermal degradation mechanism

1. Introduction

Acrylic and methacrylic polymers are being widely used in modern technological processes. Stabilisers are used to prevent the degradation of polymers and thereby, to effectively extend their useful lifetime. In the case of acrylic and methacrylic polymers, the main function of these materials is to deactivate the radicals formed from the random scission of the main chain after thermal activation. In general, the stabilisers do not completely eliminate the decomposition but they retard the auto-degradation reactions by interfering with radical depropagation [1]. There are several types of stabilisers, which are categorized according to the way they interrupt the process. The most common are hindered phenols and amines, which neutralize radicals prior to their harmful action.

Subsequent to the discovery by Kratschmer et al. [2] of a method for the macroscopic synthesis of fullerene C_{60}, the chemical properties of this fascinating molecule have been intensively investigated [3]. Fullerenes are highly electronegative molecules and can act as electron accepting substances in the presence of potent electron donors such as radicals. The multifunctional character

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Table 1
Molecular weight characteristics and glass transition temperature of PAA-*n* and PMA-*n*

	$M_w \times 10^{-3}$[a]	$M_n \times 10^{-3}$[a]	M_w/M_n[a]	T_g[b] (°C)
PAA-4	111	30	3.7	−49
PAA-5	111	34	3.3	−58
PAA-6	124	32	3.9	−61
PAA-7	109	30	3.6	−66
PMA-4	141	37	3.8	30
PMA-5	247	52	4.7	−14
PMA-6	134	32	4.2	−21
PMA-7	119	27	4.4	−25

[a] Determined by SEC.
[b] Obtained by DSC.

of C_{60} allows it to accept many reactive entries. Fullerenes have low aromatic properties, on the other hand adducts are more aromatic and, therefore, are very stable [4].

In this work we investigated the influence of additives of fullerene C_{60} on thermal behaviour and thermodegradation of poly-*n*-alkyl acrylates (PAA-*n*), from butyl to heptyl, and of corresponding poly-*n*-alkyl methacrylates (PMA-*n*) by thermogravimetry in dynamical conditions and pyrolysis/gas chromatography techniques in isothermal conditions. The aim of this study was to take advantage of the unique properties of fullerene C_{60} and explore its potential applications as stabiliser in the thermal degradation of acrylic polymers, essentially characterized by radical processes [5].

2. Experimental

2.1. Materials

The polymerisation of *n*-alkyl acrylates and *n*-alkyl methacrylates was carried out on bulk samples in argon atmosphere in the presence of benzoyl peroxide (0.2 wt%) at 70 °C for 24 h. All monomers were commercially available from Reaxim (Russia) with the exception of *n*-heptyl methacrylate which was synthesized from methacrylic acid and heptyl alcohol.

Size exclusion chromatography (SEC) analyses were carried out in THF using a KhCh-1039 liquid chromatograph (Russia) equipped with a 0.5 × 400 mm column, sorbent Ultrastyragel (10^3, 10^4, and 10^5 Å pore size) and home made UV (260 nm) detector [6]. The system was calibrated using a set of narrow polystyrene standards with molar mass ranging from 400 to 1×10^6 Da. Differential scanning calorimetry (DSC) scans were carried out on a Perkin–Elmer Pyris 1 instrument. Typically, ca. 10 mg of polymer was analysed in each run, while scan rate was 20 °C/min under helium. The molecular weight characteristics and the glass transition temperature of PAA-*n* and PMA-*n* are reported in Table 1.

Fullerene C_{60} (purity 99.5%) was donated by ZOO "ILIP" (Russia). In a typical preparation of mixture (polymer + fullerene), 100 mg of polymer was dissolved in toluene (4 ml) and mixed with 2 ml of toluene solution of C_{60} with concentration 0.5 mg/ml. After evaporation of the solvent in vacuum, the samples were dried for three days in vacuum (1 mmHg) at 50 °C. The content of fullerene C_{60} in the mixtures was about 1% wt. This mixing preparation produces homogeneous samples with non-covalent interactions between the components [4].

2.2. Thermal analysis

Dynamic thermogravimetric analyses (TGA) were performed on a Perkin–Elmer TGA-7 instrument with platinum pan using 5 mg of polymer as probe. The samples were heated at 10 °C/min in nitrogen atmosphere with a flow rate of 60 ml/min. TGA and derivative thermogravimetry (DTG) curves were recorded from 50 to 600 °C. Every entry in the Tables 2 and 3 is the averaged value obtained from two or three repeated measurements. Experimental error is about ±1 °C and ±0.3% for thermal degradation temperature and residue yield, respectively.

2.3. Degradation procedure

The thermal degradation experiments were carried out by pyrolysis–gas chromatography and pyrolysis–gas chromatography/mass spectrometry techniques using a Chemical Data System Pyroprobe 2000 apparatus equipped with a platinum coil. The sample (0.4–0.5 mg) was placed in a quartz tube secured with plugs of quartz wool and inserted into the coil filament of the Pyroprobe. The probe was connected, through an interface maintained at 200 °C, into the injector of a Hewlett-Packard 6890 Plus gas chromatograph equipped with

Table 2
TGA results for PAA-*n*

	PAA-*n*				PAA-*n* + fullerene			
	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 4$	$n = 5$	$n = 6$	$n = 7$
T_{max} (°C)	409	407	411	402	410	411	412	405
Residue[a] (%)	3.4	3.1	3.3	2.2	6.2	6.0	5.3	3.8

[a] Value calculated as (100 wt% − wt% loss at 600 °C).