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Microwave-assisted preparation and thermal properties of polymethacrylates with brominated carbazolyl pendant groups

RAPID COMMUNICATION

Summary — A series of polymethacrylates containing brominated carbazolyl pendant groups was obtained by using microwave irradiation in the synthesis of monomers. The modified methacrylates were polymerized in toluene as solvent with AIBN as initiator. TGA showed the bromo-derivatives to have higher initial decomposition temperatures (IDT) as compared with the IDT of the original polymer containing no bromine. Thermal stability of the bromo-derivatives was found to be related to the number of bromine atoms introduced into the carbazole ring and to rise in the ascending order: 3-Br < 3,6-di-Br < 1,3,6-tri-Br. The 1,3,6-tri-Br derivative was found to exhibit the maximum IDT temperature difference, *viz.*, 40°C.

Key words: bromination, carbazole, microwave irradiation, polymethacrylates, thermal stability.

The carbazole group is one of the most interesting chromophores in photochemistry and has been the subject of many investigations. Particularly, poly(*N*-vinyl-carbazole) (PVCz) has been applied in a number of devices, for instance, as a photoreceptor in electrophotographic recording materials such as copying films or offset printing plates [1]. Recently, PVCz has attracted attention in applications related to organic light-emitting diodes (LEDs), in which the emitting layer is formed by PVCz itself [2–5] or PVCz blended with other materials [6]. Such devices have shown a remarkable increase in luminescence efficiency and relatively facile color tunability [7]. Other *N*-carbazole-containing polymers have been shown to exhibit a similar hole transport [8, 9] and photo- and electroluminescent (EL) properties in spite of the lower content of carbazole chromophores [10].

In a search for the development of polymeric electroluminescent materials [11, 12] that can be used as an alternative to PVCz, we have decided to prepare and exploit thermal properties of four *N*-carbazole-containing polymers. Since substitution of heavy atoms with aromatic rings causes drastic enhancement of the singlet-triplet intersystem crossing and gives different electroluminescent colors of the emitting layer [5, 13], at this stage of the investigation we have chosen poly(2-carbazolyethyl methacrylate) (PCEM) and its

mono-, di- and tribromo derivatives (Fig. 1) as potential materials for electronic applications.

We also report on the application of microwave heating at the stage of monomer synthesis, which resulted in substantial reduction of reaction times. The application of microwave irradiation is already a well-established procedure for performing chemical conversions, and its main advantage lies in heating rates much higher than those achieved by conventional modes [14–17].

The starting material for monomer synthesis, 9-(2-hydroxyethyl)carbazole, was synthesized from carbazole and ethylene carbonate by refluxing them in DMF under microwave irradiation for 12 min. A trace amount of NaOH was added to the reaction mixture. The brominated derivatives of carbazole were prepared by heating carbazole used in an appropriate mole ratio with a 40% HBr solution and a 30% H₂O₂ solution under microwave irradiation for 20 min. Then, the brominated carbazoles were converted into *N*-(2-hydroxyethyl) derivatives in the reaction with ethylene carbonate. Finally, the *N*-(2-hydroxyethyl) derivatives were transformed into methacrylate esters by the reaction with methacryloyl chloride in 1,2-dichloroethane and pyridine in the presence of a trace amount of hydroquinone. The polymerization reactions of all the monomers were performed in toluene solutions in the presence of AIBN as an initiator (Fig. 1).

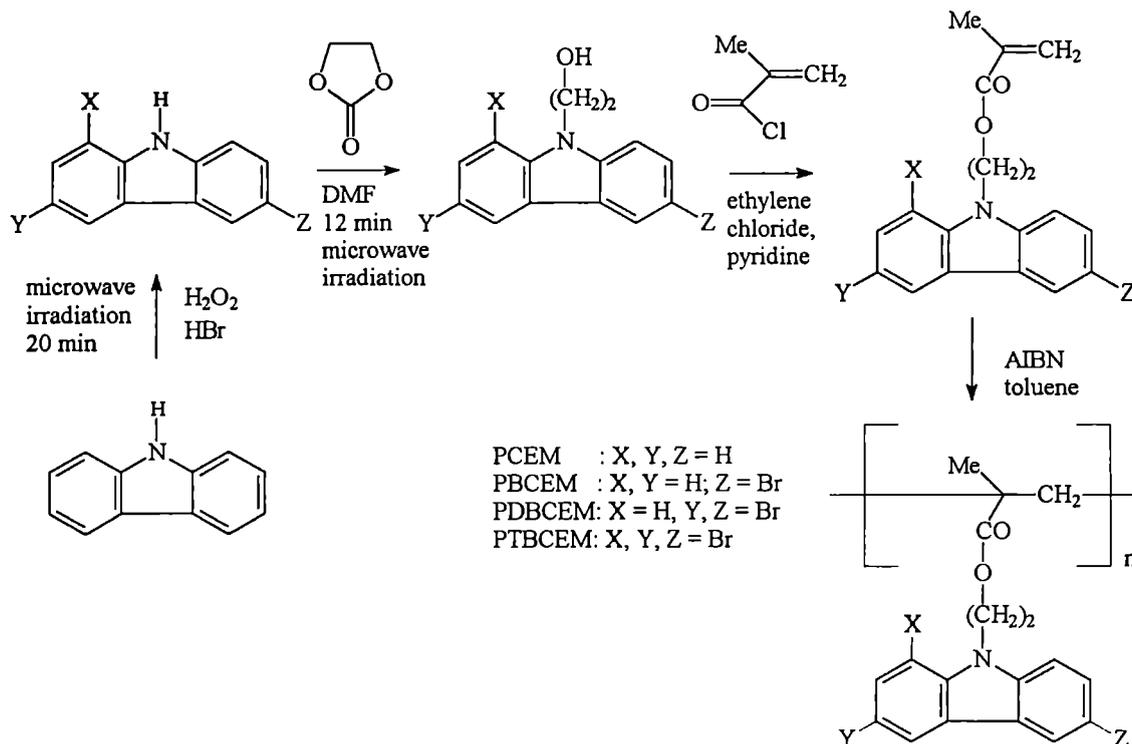


Fig. 1. Preparation of poly[2-(9-carbazolyl)ethyl methacrylate] (PCEM) and its derivatives

The molecular weights of the polymers were estimated in THF by gel permeation chromatography (GPC) by using polystyrene as standard to give mass and number average weights shown in Table 1.

Table 1. Number and weight average molecular weights of the polymers

Polymer	$M_n \cdot 10^{-4}$	$M_w \cdot 10^{-4}$	M_w/M_n
PCEM	1.59	4.02	2.54
PBCEM	1.47	3.36	2.28
PDBCEM	1.83	3.79	2.07
PTBCEM	1.05	1.20	1.15

Thermogravimetric analysis (TGA) showed the bromo-derivatives to have higher initial decomposition temperatures (IDTs) as compared with the pristine polymethacrylate with carbazolyl pendant groups without bromine (Fig. 2). Thermal stability was found to depend on the number of bromine atoms incorporated into the aromatic ring and to rise in the following order: 3-Br < 3,6-di-Br < 1,3,6-tri-Br; with the 1,3,6-Br, the IDT temperature difference reaches a maximum value of 40°C. Previous studies [18–21] allow to assume that the halogen atom introduced into the carbazole ring influences radical stability, which would in turn delay the overall rate of the decomposition process.

Further investigations on the polymers properties, evaluation and optimization of their performance are still in progress and will be published in a full paper.

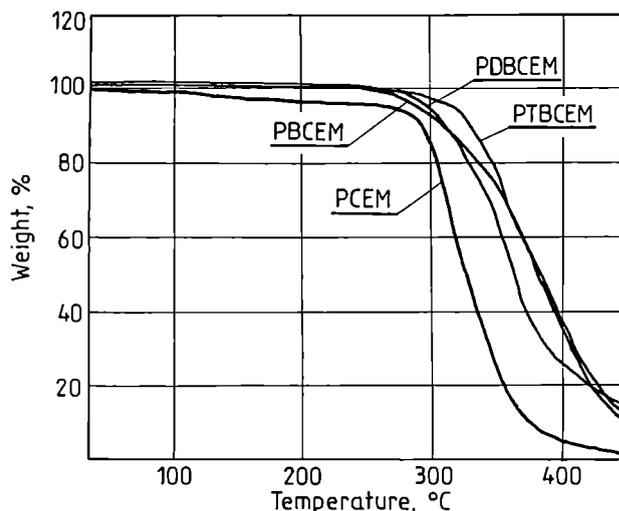


Fig. 2. Thermogravimetric analysis of PCEM, PBCEM, PDBCEM, PTBCEM at 10 K/min

EXPERIMENTAL

Bromination of carbazole and synthesis of *N*-(2-hydroxyethyl)carbazoles were carried out in the Synthwave 402 (Prolabo) microwave reactor.

Polymerization: The monomers were taken in a desired mole ratio and dissolved in toluene; AIBN (1%) was added as initiator. The reaction mixture was flushed with argon for 20 min and then heated in a water bath at 60°C to initiate polymerization. After 48 hrs the reaction was terminated and a large amount of methanol

was added to precipitate the polymer. The product was redissolved several times in THF and reprecipitated with methanol.

Thermogravimetric analysis was performed in a Netzsch TG-209 thermogravimetric analyzer, operated in a dynamic mode at a heating rate of 10 K/min. The conditions were: sample mass ~1.5 mg, atmosphere — argon, flow rate — 30 cm³/min, temperature range: 30—450°C.

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