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Synthesis and polymerization of alkyl methacrylates carrying carbazolyl pendant groups

RAPID COMMUNICATION

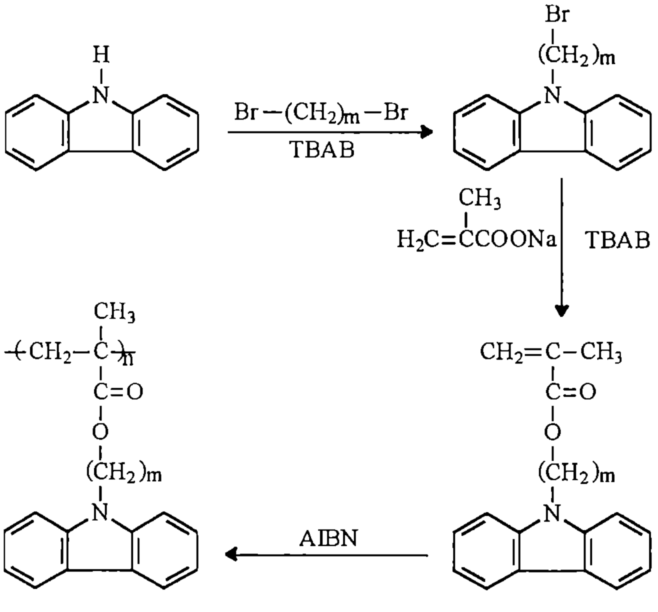
Summary — Four monomers, *viz.*, ω-(9-carbazolyl)alkyl methacrylates, were prepared from 9-(ω-bromoalkyl)carbazoles and alkali metal salts of methacrylic acid. The methacrylates were polymerized in toluene by using azobisisobutyronitrile (AIBN) as initiator. Molecular weights of the resulting polymers were established by gel permeation chromatography (GPC) (Table 2). Photoluminescence spectra were recorded for the four synthesized polymers in the solid state and for poly(vinyl carbazole). The spectra were found to be comparable, the intensity of emission was found to be related to the number of carbon atoms in the alkyl chain (C2—C6) and to increase as the length of the chain was increased.

Key words: ω-(9-carbazolyl)alkyl methacrylates, radical polymerization, photoluminescence spectra.

Carbazole is a prototypical organic molecule that has shown a potential for technological applications. Polymers based on this molecule have good electro- and photo-active properties on account of their high hole transporting mobility, strong absorption in the ultraviolet spectral region and blue light emission. In the xerographic industry the use of such polymers as photoconductive charge-transport layers has also been considered [1]. Recently, poly(N-vinylcarbazole) (PVK) has attracted attention in applications related to organic light-emitting diodes (LEDs) in which the emitting layer is formed by PVK itself or blended with other materials. Such systems have shown a remarkable increase in luminescence efficiency as compared with those into which PVK was not incorporated [2].

However great deal has been published on the properties and behavior of PVK, there is only a limited number of papers on the synthesis and properties of other polymers in which the carbazolyl group is separated from the polymer backbone by two or more atoms [3]. Since carbazole derivatives are the main subject in this laboratory, we have decided to obtain and to characterize a series of new polymers containing a carbazole block within their structures.

In this report it is demonstrated that poly[ω-(9-carbazolyl)alkyl methacrylates] with different lengths of the alkyl spacer between the carbazolyl group and the polymer backbone can be prepared by radical polymeri-



m = 2, 4, 5, 6.

Fig. 1. Synthetic route to poly[ω-(9-carbazolyl)alkyl methacrylates]

Table 1. Characterization of ω-(9-carbazolyl)alkyl methacrylates

Monomer	Mp., °C	IR (KBr), cm^{-1}	^{1}H-NMR ($CDCl_3$, TMS), ppm	Anal., %
2-(9-Carbazolyl)ethyl methacrylate	81.5—82.5	720, 746 (s), 816 (m), 949 (m), 1157 (m), 1172 (s), 1318 (s), 1456 (s), 1489 (w), 1598 (w), 1630 (m), 1720 (s), 2978 (m), 3051 (m)	1.79—1.82 (s, 3 H, -CH_3), 4.53—4.60 (m, 4 H, -CH_2-CH_2-), 5.45—5.49 (m, 1 H, =CH_2 trans), 5.91—5.94 (s, 1 H, =CH_2 cis), 7.13—7.50 (m, 6 H, aromatic ring 1, 2, 3, 6, 7, 8), 8, 03—8.15 (m, 2 H, aromatic ring 4,50)	calcd. for $C_{18}H_{17}NO_2$: C 77.4, H 6.1, N 5.0; found C 77.2, H 6.0, N 5.0
4-(9-Carbazolyl)butyl methacrylate	liquid	724 (s), 751 (s), 816 (m), 942 (m), 1015 (m), 1167 (s), 1240 (m), 1297 (m), 1326 (s), 1454 (s), 1484 (m), 1597 (m), 1630 (m), 1716 (s), 2878 (m), 2957 (s), 3023 (w), 3051 (m)	0.99—1.93 [m, 4 H, -$(CH_2)_2$-(2'—3')], 1.9—2.0 (s, 3 H, CH_3), 4.08—4.36 (m, 4 H, -OCH_2-, -NCH_2-), 5.53 (m, 1 H, =CH_2 trans), 6.06 (s, 1 H, =CH_2 cis), 7.19—7.49 (m, 6 H, aromatic ring 1, 2, 3, 6, 7, 8), 8.04—8.16 (m, 2 H, aromatic ring 4, 5)	calcd. for $C_{20}H_{21}NO_2$: C 78.1, H 6.9, N 4.6; found C 78.2, H 6.8, N 4.5
5-(9-Carbazolyl)pentyl methacrylate	liquid	724 (s), 750 (s), 815 (m), 940 (m), 1167 (s), 1298 (m), 1326 (s), 1454 (s), 1484(m), 1597 (m), 1630 (m), 1716 (s), 2865 (m), 2937 (s), 3052 (w)	0.98—1.92 [m, 6 H, -$(CH_2)_3$-(2'—4')], 1.9—2.0 (s, 3 H, CH_3), 4.08—4.30 (m, 4 H, -OCH_2-, -NCH_2-), 5.52 (m, 1 H, =CH_2 trans), 6.06 (s, 1 H, =CH_2 cis), 7.19—7.49 (m, 6 H, aromatic ring 1, 2, 3, 6, 7, 8), 8.03—8.16 (m, 2 H, aromatic ring 4, 5)	calcd. for $C_{21}H_{23}NO_2$: C 78.5, H 7.2, N 4.4; found C 77.9, H 7.3, N 4.2
6-(9-Carbazolyl)hexyl methacrylate	liquid	724 (s), 751 (s), 815 (m), 940 (m), 1167 (s), 1233 (m), 1297 (m), 1326 (s), 1461 (s), 1485(s), 1597 (m), 1629 (m), 1716 (s), 2861 (m), 2935 (s), 3052 (m)	0.97—1.89 [m, 8 H, -$(CH_2)_3$-(2'—5')], 1.9—2.0 (s, 3 H, CH_3), 4.08—4.26 (m, 4 H , -OCH_2-, -NCH_2-), 5.51 (m, 1 H, =CH_2 trans), 6.06 (s, 1 H, =CH_2 cis), 7.17—7.46 (m, 6 H, aromatic ring 1, 2, 3, 6, 7, 8), 8.02—8.13 (m, 2 H, aromatic ring 4, 5)	calcd. for $C_{21}H_{23}NO_2$: C 78.8, H 7.5, N 4.2; found C 78.6, H 7.5, N 4.3

zation from readily available ω-(9-carbazolyl)alkyl methacrylates (Fig. 1). Preliminary investigations have shown the polymers to exhibit luminescence properties similar to those of PVK.

RESULT AND DISCUSSION

Four monomers, ω-(9-carbazolyl)alkyl methacrylates, were prepared from 9-(ω-bromoalkyl)carbazoles and sodium salts of methacrylic acid. The starting com- pounds for the synthesis of monomer [*e.g.*, 9-(bromoalkyl)carbazoles] were obtained by the alkylation reaction of carbazole with an excess of α,ω-dibromoalkane under phase-transfer catalysis conditions. The alkyl spacers in the monomers were designed to contain 2, 4, 5 and 6 carbon atoms. In order to purify and separate the monomers from unreacted 9-(bromoalkyl)carbazole, 2-(9-carbazolyl)ethyl methacrylate was recrystallized several times from ethanol, while others were subjected to column chromatography. The synthetic route for the preparation of the monomers is depicted in Figure 1, whereas their properties are listed in Table 1.

Table 2. Molecular weights of synthesized methacrylate polymers

Polymer	$\overline{M}_n$	$\overline{M}_w$	P_d
Poly[2-(9-carbazolyl)ethyl methacrylate]	11 200	36 400	3.27
Poly[4-(9-carbazolyl)butyl methacrylate]	12 500	34 300	2.76
Poly[5-(9-carbazolyl)pentyl methacrylate]	12 900	28 500	2.20
Poly[6-(9-carbazolyl)hexyl methacrylate]	12 400	28 100	2.62

ω-(9-Carbazolyl)alkyl methacrylates were polymerized by using AIBN (1 mole %) as an initiator in toluene in highly evacuated ampules at 60°C for 48 h. The polymers were precipitated from methanol and purified by repeated precipitations from THF solution from methanol. The molecular weights were established in THF by gel permeation chromatography (GPC) by using polystyrene as a standard to mass and number average molecular weights shown in Table 2.

Four prepared polymers were the subject of preliminary investigation that were carried out in order to compare the photoluminescence properties of the methacrylates against PVK in the solid state. Solid state photoluminescence spectra were measured for polymer films that were a few micrometers in thickness. The

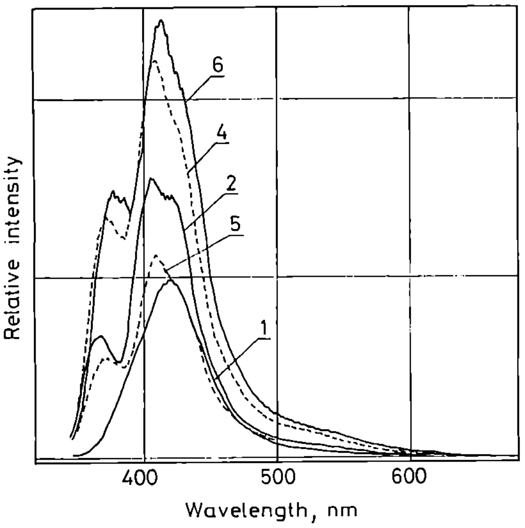


Fig. 2. Fluorescence spectra of films of poly[ω-(9-carbazolyl)alkyl methacrylates] and PVK. The excitation wavelength is 340 nm: 1 — PVK, 2 — poly[2-(9-carbazolyl)ethyl methacrylate], 4 — poly[4-(9-carbazolyl)butyl methacrylate], 5 — poly[5-(9-carbazolyl)pentyl methacrylate], 6 — poly[6-(9-carbazolyl)hexyl methacrylate]

films were obtained from their solutions in THF at room temperature followed by drying at 40°C in vacuum for 1 day. The spectra of all the polymers and PVK are presented in Fig. 2.

As can be seen in Figure 2, in the solid state the photoluminescence intensities of the four synthesized poly[ω-(9-carbazolyl)alkyl methacrylates] and PVK are comparable. Moreover, it seems that the intensity of emission depends on the number of atoms in the alkyl chains and increases with the length of the spacers. Whereas the intensities of PVK and poly[2-(9-carbazolyl)ethyl methacrylate] are in the same range, the emissions of poly[4-(9-carbazolyl)butyl- and [6-(9-carbazolyl)hexyl methacrylates] are stronger than is PVK emission. The only exception to this rule is poly[5-(9-carbazolyl)pentyl methacrylate] which exhibits a weaker emission than does poly[2-(9-carbazolyl)ethyl methacrylate]; however, it is still stronger than PVK.

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

EXPERIMENTAL

9-(ω-Bromoalkyl) carbazoles

Carbazole (3.34 g, 20 mmols) was added to an intensively stirred boiling mixture of α,ω-dibromoalkane (100 mmols), cyclohexane (100 ml), tetrabutylammonium bromide (0.64 g, 2 mmols), and K_2CO_3 (22.11 g, 160 mmols). Stirring was continued under reflux for 6 h. Then the mixture was filtered and the solvent was evaporated. The residue was distilled in the Kugelrohr apparatus to remove the excess of α,ω-dibromoalkane and finally purified by Al_2O_3 column chromatography (eluent: hexane). The product was crystallized from methanol to give white crystals (yield: 59—67%).

ω-(9-Carbazolyl)alkyl methacrylates

A mixture of a chloroform solution (20 ml) of 9-(ω-bromoalkyl)carbazoles (10 mmols), tetrabutyloammonium bromide (2 mmols, 0.64 g) and a 40% aqueous solution [containing 40 mmols (4.32 g)] of sodium methacrylate in the presence of trace amounts of hydroquinone was reacted at 55°C for 24 h. The layers were separated and washed three times with a 5% solution of NaOH, and then twice with distilled water. The lower layer was dried over magnesium sulfate and evaporated to remove the chloroform. The residue was then purified by Al_2O_3 column chromatography (eluent: hexane) (yield: 77—83%).

REFERENCES

1. Nespurek S.: *Synth. Met.* 1993, **61**, 55.
2. Wang G., Yuan C., Wu H., Wei Y.: *J. Appl. Phys.* 1995, **78**, 2679; Romero D. B. Shaer M., Leclerc M., Ades D., Siove A., Zuppiroli L: *Synthetic Metals* 1996, **80**, 261; Hu B., Yang Z., Karasz F. E.: *J. Appl. Chem.* 1994, **76**, 2419.
3. Hu Ch. J., Oshima R., Sato S., Seno M.: *J. Polym. Sci., Part C, Polym. Lett.* 1988, **26**, 441; Oshima R., Uryu T., Seno M.: *Macromolecules* 1987, **18**, 1043; Oshima R., Biswas M., Wada T., Uryu T.: *J. Polym. Sci., Part C, Polym. Lett.* 1985, **23**, 151; Ito S., Ohmori S., Yamamoto M.: *Macromolecules* 1992, **25**, 185.

Received 24 VII 1998