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Synthesis and aqueous solution characterization of amphiphilic diblock copolymers containing carbazole

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Abstract

A series of near-monodisperse diblock copolymers of 2-(*N*-carbazolyl)ethyl methacrylate and 2-(dimethylamino)ethyl methacrylate (DMAEMA) of relatively low molecular weights (2600–24,000 g mol^{-1}) were synthesized by group transfer polymerization using tetrahydrofuran (THF) as a solvent. The molecular weight distributions and compositions of all the copolymers were obtained using gel permeation chromatography (GPC) in THF and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy, respectively. Differential scanning calorimetry and thermal gravimetric analysis provided low glass transition temperatures (T_gs) of about 60 °C and decomposition temperatures between 320 and 450 °C for the copolymers, respectively. The three copolymers with the highest DMAEMA content were water-soluble below pH 7. Aqueous GPC at pH 3 showed that the water-soluble block copolymers formed micelles with apparent number average molecular weights above 100,000 g mol^{-1}.

Keywords: Group transfer polymerization; 2-(*N*-carbazolyl)ethyl methacrylate; 2-(dimethylamino)ethyl methacrylate

1. Introduction

Amorphous organic photorefractive polymer systems are new materials with potential application as recording media for holographic storage and for real-time optical information processing [1]. These systems are usually mixtures containing various components with different functions, such as charge transport, hole transport, and electro-optical properties. Carbazole-containing polymers, and, in particular, poly(*N*-vinylcarbazole), are usually used as the charge transporting component. Poly(*N*-vinylcarbazole) has also been used in photocopiers [2] and in light-emitting diodes [3,4].

Despite the successful use of carbazole-containing polymers in the above applications, these polymers lack size homogeneity and are characterized by a broad molecular weight distribution (MWD). Moreover, carbazole-containing polymers require processing in organic solvents, because they are particularly hydrophobic and their aqueous processing is precluded. The aim of the present investigation is to address both of these issues and provide water-soluble polycarbazoles of a narrow MWD. Thus, block copolymers based on a carbazole-containing monomer, 2-(*N*-carbazolyl)ethyl methacrylate (CbzEMA), and a hydrophilic monomer, 2-(dimethylamino)ethyl methacrylate (DMAEMA), were prepared by group transfer polymerization (GTP) [5–7] and were characterized by a variety of techniques.

2. Results and discussion

While DMAEMA is commercially available, CbzEMA was synthesized in two steps [8,9], according to Scheme 1. Thus, carbazole was reacted with an excess (10%) of ethylene carbonate in refluxing dimethylformamide (DMF) in the presence of a small amount of NaOH, to give 2-(*N*-carbazolyl)ethanol at ca. 60% yield. This was purified by three recrystallizations in a 1:1 benzene/cyclohexane mixture [10], and it was subsequently reacted to an excess (10%) of methacryloyl chloride in dichloromethane in the presence of triethylamine at room temperature to give CbzEMA in nearly quantitative yield (ca. 90%). CbzEMA was purified by three recrystallizations in methanol.

A series of DMAEMA–CbzEMA diblock copolymers were prepared using GTP [5–7] at room temperature. The initiator used was 1-methoxy-1-trimethylsiloxy-2-methyl-1-propene (MTS), while tetrabutylammonium bibenzoate (TBABB) [7] served as the polymerization catalyst. Tetrahydrofuran (THF) was used as the solvent. The block copolymerizations were accomplished by the sequential

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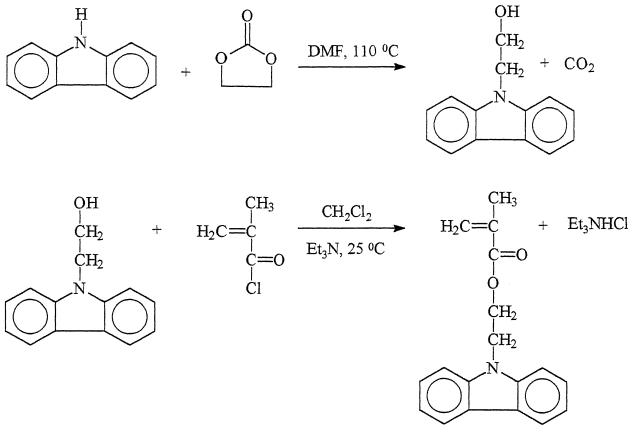


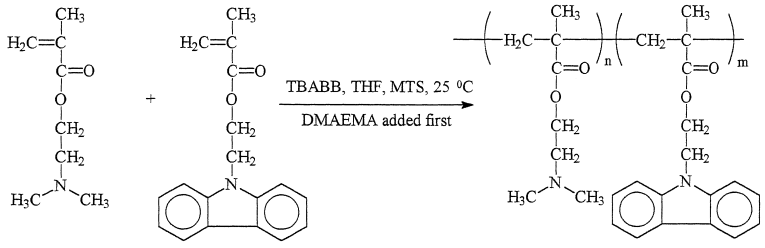
Scheme 1. Synthesis of the CbzEMA monomer from carbazole, ethylene carbonate, and methacryloyl chloride.

addition of DMAEMA and CbzEMA, in this order, in accord with Scheme 2. It was determined that it was less efficient to polymerize CbzEMA first as this led sometimes to no polymerization at all. This can be attributed to small amounts of protonic impurities in CbzEMA, which can terminate the polymerization. Such impurities are not present in the DMAEMA monomer, a liquid, which is contacted with the powerful drying agent calcium hydride, a solid, followed by distillation. The solid-state of the CbzEMA monomer precludes its facile processing with calcium hydride. Instead, the purification of CbzEMA relies exclusively on recrystallization. CbzEMA behaves better as second than first monomer possibly, because 'living' DMAEMA homopolymer is a better (and faster) initiator for CbzEMA than MTS.

Quantitative yields were obtained in all polymerizations. The polymers were recovered from their polymerization solutions by precipitation with *n*-hexane, followed by vacuum drying. The prepared polymers, their molecular weight (MW) characteristics, and their compositions are presented in Table 1. Three block copolymers with DMAEMA/CbzEMA molar ratios of 2, 4, and 10 were synthesized. One CbzEMA homopolymer and one statistical copolymer of CbzEMA and DMAEMA were also prepared. The number average MWs (M_ns) and polydispersity indices (PDIs, M_w/M_n) were determined by gel permeation chromatography (GPC) in THF (PMMA standards, RI detector, polymer laboratories PL mixed 'E' column). The M_ns increased with the theoretical MWs, calculated from the monomer-to-initiator ratio, but the values of the former were systematically higher than those of the latter due to hydrodynamic differences between the CbzEMA and DMAEMA units and the MMA units of the MW calibration standards, and possibly due to partial initiator deactivation. The PDIs were relatively low (<1.3) in all cases, indicating an improved size homogeneity compared to that of commercial poly(*N*-vinylcarbazole) (PDI > 3) and polyCbzEMAs prepared by free radical polymerization (PDI ~ 3) [11]. It is noteworthy that the PDIs of random copolymers of 2-(*N*-carbazolyl)ethyl acrylate with methyl acrylate or *n*-butyl acrylate prepared by GTP ranged between 1.45 and 3.41 [12], while those of norbornene-based carbazole-containing homopolymers and block copolymers synthesized by living ring-opening metathesis polymerization (ROMP) were 1.22–1.46 [13].

The polymers were characterized by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy (300 MHz AVANCE Bruker spectrometer) in deuterated chloroform ($CDCl_3$). Fig. 1 shows the ^{1}H NMR spectra of the CbzEMA (a) and DMAEMA (b) homopolymers, as well as that of the $DMAEMA_{10}$-*b*-$CbzEMA_5$ block copolymer (c). The peak assignments are shown in the spectra. Peaks e and k were chosen as the characteristic peaks for polyCbzEMA and polyDMAEMA, respectively. The copolymer compositions were determined from the ratio of the areas under the signals of the characteristic peaks in the copolymer ^{1}H NMR spectra. These compositions are presented in Table 1 and agree well with the theoretical ones, based on the comonomer feeds, also shown in the table.

Differential scanning calorimetry (DSC) measurements (DSC 2910 calorimeter from TA Instruments, scanning rate 20 °C min^{-1}, two scans) provided the glass transition temperatures, T_gs (taken at the second scan), of the polymers. The T_g of the $CbzEMA_5$ homopolymer was determined to be 88 °C, which is lower than the values of 131 °C [11] and 146 °C [14] reported in the literature for high MW (M_n > 20,000 g mol^{-1}) CbzEMA homopolymers. The T_gs of the block copolymers were found to be even lower (single values), around 60 °C, suggesting no microphase separation of the two blocks in the solid state, which can be attributed again to the low MW of the copolymers. The T_g of DMAEMA homopolymer is ~ − 10 °C [15]. It is noteworthy that the T_g of the random copolymer was even



Scheme 2. Synthesis of DMAEMA–CbzEMA diblock copolymers by sequential GTP.

Table 1
Molecular weights, polydispersities, and copolymer compositions of the CbzEMA–DMAEMA copolymers determined using GPC and ^{1}H NMR spectroscopy

Polymer number	Polymer formula	Theoretical[a] MW	GPC in THF[b]		GPC in water at pH 3.0[c]		Theoretical CbzEMA content (mol%)	Actual CbzEMA content (mol%)[d]
			M_n	M_w/M_n	M_n	M_w/M_n		
1	$(CbzEMA)_5$	1495	2810	1.11	Water-insoluble		100	100
2	$(DMAEMA)_5$-*b*-$(CbzEMA)_5$	2280	2570	1.28	Water-insoluble		50	54
3	$(DMAEMA)_{10}$-*b*-$(CbzEMA)_5$	3065	6840	1.19	Water-insoluble		33	38
4	$(DMAEMA)_{10}$-*co*-$(CbzEMA)_5$[e]	3065	7300	1.11	30,000	3.17	33	36
5	$(DMAEMA)_{20}$-*b*-$(CbzEMA)_5$	4635	10,300	1.10	176,800	1.67	20	23
6	$(DMAEMA)_{50}$-*b*-$(CbzEMA)_5$	9345	23,600	1.10	108,600	2.27	9.1	12

[a] Initiator fragment (100 g mol^{-1}) included.
[b] PMMA standards, PL mixed E column, RI detector.
[c] PEG standards, Superdex column, pH 3 in 0.1 M malonic acid buffer and 1.0 M $NaNO_3$, RI detector.
[d] As determined by ^{1}H NMR spectroscopy in $CDCl_3$.
[e] Random copolymer.

lower, around 35 °C. The low T_gs of the present polymers can be advantageous for their thermal processing and also for the low-temperature orientation of the carbazole units in an electric field. Thermal gravimetric analysis (TGA) measurements (TGA 2950 analyzer from TA Instruments) were performed to determine the decomposition temperatures for the copolymers. While the copolymers start losing weight at ~320 °C and lose most of their weight at ~450 °C, the carbazole homopolymer decomposes between 390 and 440 °C, reflecting the thermal stability of the carbazole units. The thermal decomposition range of methacrylate homopolymers of an electron acceptor, 2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate, measured using the same instrument, were found to be lower, between 320 and 370 °C [16].

The presence of hydrophilic, ionizable DMAEMA units confers water-solubility to some of the copolymers. In particular, copolymers 4, 5, and 6 (most hydrophilic, Table 1)

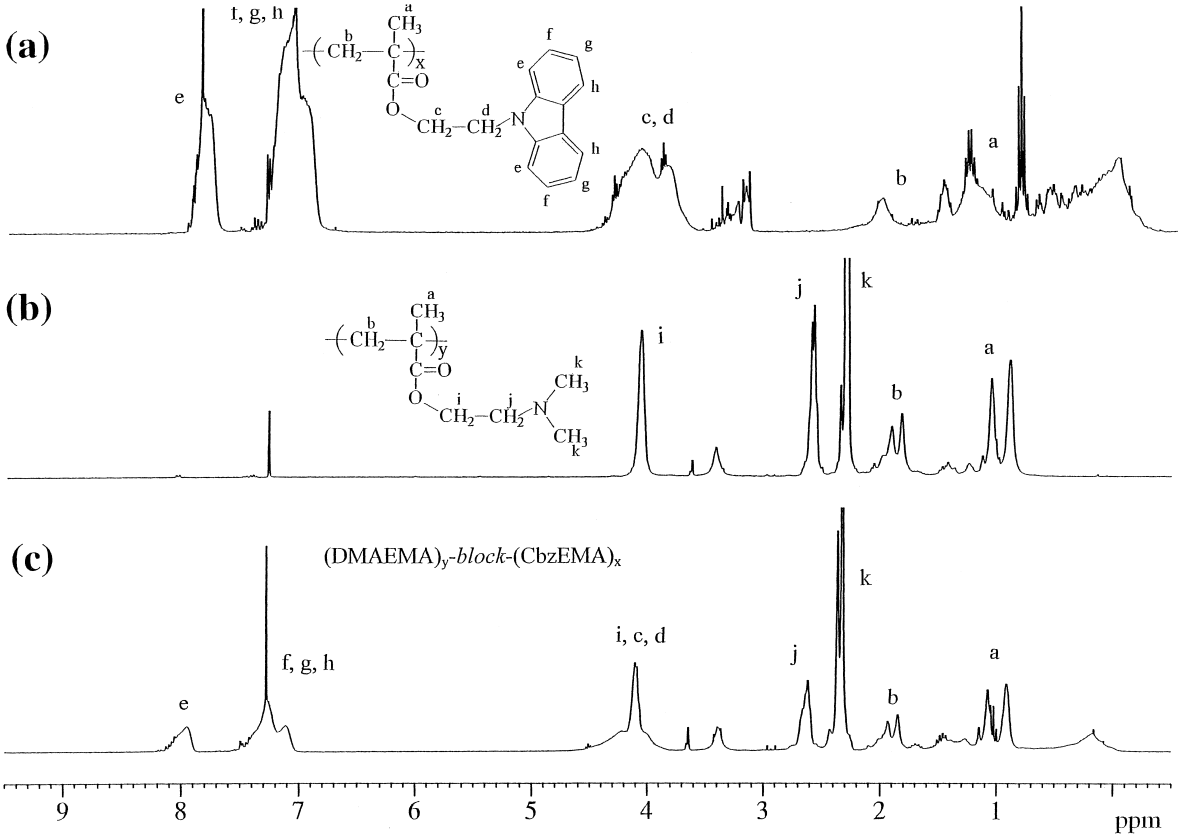


Fig. 1. Proton NMR spectra of (a) the $(CbzEMA)_5$ homopolymer, (b) the $(DMAEMA)_{20}$ homopolymer, and (c) the $(DMAEMA)_{10}$-*b*-$(CbzEMA)_5$ diblock copolymer.

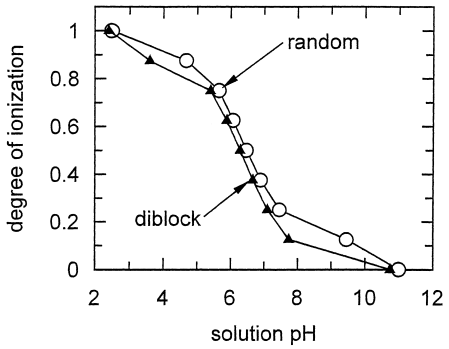


Fig. 2. Hydrogen ion titration curves of the two isomeric copolymers, the diblock copolymer $(DMAEMA)_{10}$-*b*-$(CbzEMA)_5$ and the statistical (random) copolymer $(DMAEMA)_{10}$-*co*-$(CbzEMA)_5$.

gave clear 1% w/w aqueous solutions at pH 2, while copolymers 2 and 3, under the same conditions, were dispersed to turbid, but stable suspensions. This water-solubility and dispersibility of the copolymers makes possible their aqueous processing, which can be important for the environmentally friendly handling of carbazole-containing polymers for the large-scale manufacture of inexpensive electronic components. However, above pH 7.5, where the DMAEMA units lose most of their charge (see next paragraph), the aqueous solutions of copolymers 4, 5, and 6 become turbid and finally precipitate.

Fig. 2 shows the hydrogen ion titration curves of the two isomeric copolymers with the same DMAEMA/CbzEMA composition of 2:1, but different architecture. These are the diblock copolymer $(DMAEMA)_{10}$-*b*-$(CbzEMA)_5$ and the statistical (random) copolymer $(CbzEMA)_5$-*co*-$(DMAEMA)_{10}$. The titration curves of the two copolymers are almost identical, indicating that the copolymer architecture does not affect significantly their hydrogen ion equilibrium properties, in agreement with previous studies [9]. The effective p*K*s (pH at 50% ionization) of the two copolymers were around 6.3; this is lower than that of DMAEMA homopolymer, which is around 7.3 [9]. This difference can be attributed to the presence of the hydrophobic carbazole units in the copolymers, which lowers the local dielectric constant, accentuates Coulomb's law, and makes more difficult the further ionization of the DMAEMA units, rendering them less basic.

The presence of the hydrophobic carbazole group in the copolymers also leads to micellization in water [17]. The aggregation behavior of the copolymers was studied using aqueous GPC (0.1 M malonic acid buffer at pH 3, 1.0 M $NaNO_3$, PEG standards, RI detector, Pharmacia Biotech 'Superdex' column). The results are shown in Table 1. Block copolymers 5 and 6 exhibit aqueous GPC M_ns, which are several times their M_ns determined by GPC in THF. This suggests the self-assembly of the diblock copolymer chains into superstructures in water, most likely of spherical micelles, whose formation is favored by a short hydrophobic block and a longer hydrophilic one [18], as is the case with polymers 5 and 6. The actual MW of these micelles could be several times that determined by aqueous GPC due to the compact nature of spherical micelles compared to the linear PEG MW standards. Although its M_n by aqueous GPC is not as high as those of the block copolymers, random copolymer 4 also exhibits some aggregation as evidenced by the increase of its M_n in water compared to that in THF. It is noteworthy that the aggregates of this polymer are more polydisperse than those of the block copolymers, possibly reflecting a difference in the aggregate structure.

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