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Synthesis and characterization of copolymers of carbazolylalkyl(meth)acrylates and methacrylic acid

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Summary

The copolymerization of 2-(9-carbazolyl)ethylmethacrylate, 3-(9-carbazolyl)propyl-2-methacrylate and 2-(9-carbazolyl)ethylacrylate with methacrylic acid has been studied obtaining the reactivity ratios of the monomers in benzene. For the estimation of molar masses and copolymer compositions esterification of the copolymers has been performed. A thermal study of the obtained copolymers related to the carbazolylalkyl(meth)acrylate content has been carried out taking into account several theories predicting the dependence of the glass transition temperature on the copolymers composition. The copolymers in which the molar fraction of methacrylic acid did not exceed ca. 65 mol % exhibit glass transition. Glass transition temperatures increase with the increase of molar fraction of methacrylic acid.

Introduction

Carbazole-based polymers have been widely studied as components of electrophotographic and photorefractive materials as well as of electroluminescent devices. Carbazole-containing polymers soluble or dispersable in water or in aqueous alkaline media have recently attracted some attention [1,2] because of pollution problems in coating and casting by the use of organic solvents.

In this presentation we report on the synthesis and characterization of copolymers of carbazolylalkyl(meth)acrylates and methacrylic acid. Poly(methacrylic acid) is known as a polymer capable of solubilizing organic substances in water [3]. Hydrophobic modification of poly(methacrylic acid) and other polyelectrolytes can be used to enhance the scope of water-soluble macromolecules as solubilizing media [4,5]. For this reason some copolymers synthesized in this work can apparently be also used as solubilizing media for organic molecules in aqueous solutions.

Experimental

Materials

Methacrylic acid (Aldrich) was prepolymerized (UV radiation) and fractionally vacuum distilled prior to use. 2,2'-azobisisobutyronitrile (AIBN) (Aldrich) was twice recrystallized from methanol. An ethereal solution of diazomethane was prepared according to the literature [6]. The solvents, hexane, methanol, diethyl ether, dichloromethane, tetrahydrofuran, chloroform were purified by the standard procedures [7]. Benzene used for polymerizations was dried over sodium and distilled.

Synthesis

2-(9-carbazolyl)ethylmethacrylate (CEMA) (m.p. 82-83 °C) and 3-(9-carbazolyl)propyl-2-methacrylate (CPMA) (m.p. 69-70 °C) were obtained by esterification of methacryloyl chloride with 9-(2-hydroxyethyl)carbazole and 9-(2-hydroxypropyl)carbazole, respectively as described in [8]. 2-(9-carbazolyl)ethylacrylate (CEA) (m.p. 75-76 °C) was prepared by the same method using acrylolyl chloride instead of methacryloyl chloride. The crude products were purified by column chromatography with dichloromethane as eluent. 9-(2-hydroxyethyl)carbazole and 9-(2-hydroxypropyl)carbazole were prepared from carbazole and ethylene carbonate and propylene carbonate, respectively, by refluxing in dimethylformamide with the small amounts of K_2CO_3 [9]. These monomers were recrystalized from carbon tetrachloride.

Copolymerization

Copolymerizations of carbazolylalkyl(meth)acrylates and MA were performed as follows. A 20-ml benzene solution containing carbazolylalkyl(meth)acrylate and MA in a known ratio (10 mmol in total) and 0.5 mol % (on the basis of total monomers) of AIBN was repeatedly evacuated and purged with nitrogen. Polymerizations were carried out under the nitrogen blanket at 60 °C. The monomer conversion was kept under 10 %. The copolymers with high molar fraction of carbazolylalkyl(meth)acrylates were isolated and purified by precipitations from THF into hexane. The copolymers with high molar fraction of MA were isolated and purified by precipitations from methanol into diethyl ether. The copolymerizations were carried out with various mole fractions of carbazolylalkyl(meth)acrylates in monomer feed. For each initial comonomer ratio two copolymerizations were made and the average results of these experiments are shown in the Tables 1, 2 and 3. Since solubilities of carbazolylalkyl(meth)acrylates and MA homopolymers is very different and the solubility of the copolymers is different from that of the homopolymers the threefold reprecipitations yielded pure copolymers (turbidimetry).

Esterification of thus obtained copolymers was carried out as follows. To a suspension of the copolymer (0.1 g) in 100 ml of benzene 100 ml of an ethereal solution of diazomethane was added. The reaction mixture was stirred at room temperature for 24 h to result in a clear solution. In order to secure the completion of the reaction another 50 ml of the ethereal diazomethane was added, and the stirring was continued for an additional 24 h. The mixture was then concentrated by evaporation of the solvents to about one-tenth its original volume. The copolymer was precipitated by an excess of ether and purified by reprecipitating from benzene into ether three times. Finally the benzene solution was lyophilized. Complete esterification was confirmed by FTIR spectroscopy using a Bio-Rad Digilab FTS-40 spectrophotometer.

Characterization

In order to determinate the copolymer composition ^{1}H NMR spectra of the copolymers (converted into their methyl esters forms) were recorded in DMSO at room temperature by using Bruker AC 250 spectrometer. The copolymer composition was calculated from the integrals of the total aromatic and aliphatic proton regions.

For an estimation of molecular weigth GPC measurements were carried out for a $CHCl_3$ solution of the methyl ester derivatives of the copolymers (GPC traces of the acidic groups containing copolymers are broad and skewed to a higher elution volumes, implying some interactions with the column material) using a Waters system including a Waters 440 UV detector (254 nm). GPC measurements of the poly(carbazolylalkyl(meth)acrylates) were carried out using THF as eluent. Monodisperse polystyrene samples were used as standards to calculate molecular weigths of the homopolymers and copolymers in the corresponding methyl ester form. The molecular weigth of the poly(methacrylic acid) was estimated from the intristic viscosity in 0.1 N LiCl methanol solution at 26 °C and calculated by the Mark-Houwink equation [10].

The glass transition temperature measurements were carried out on a Perkin Elmer DSC-7 with a heating rate of 10 °C min^{-1}.

Results and Discussion

The copolymerization of carbazolylalkyl(meth)acrylates with MA at 60 ºC in the presence of AIBN in benzene was studied in a wide composition range with a molar fraction of CEMA, CPMA and CEA in the monomer feed ranging from 10 to 90 %. The reaction conditions and the results of these copolymerizations are shown in Tables 1-3. It is evident from the data presented in Tables 1-3 that the rate of the reactions depends on the molar ratio of the comonomers in feed and the structure of the carbazolyl-containing monomer. The time necessary for the achievement of the total monomer conversion ca. 5-10 % increases with the increase of the molar ratio [carbazolylalkyl(meth)acrylate]:[methacrylic acid]. The rate of copolymerizations in the presence of CEA is higher than that of copolymerizations in the presence of carbazolylalkylmethacrylates. The average molar mass values of the obtained copolymers are rather low and are similar to those achieved by Wainwright [1] for copolymers of N-vinylcarbazole with MA. Figure 1 shows relationship between the molar fraction of carbazolylalkyl(meth)acrylate in the feed (f_1) and the molar fraction in the copolymer (F_1) for all systems: CEMA-MA, CPMA-MA and CEA-MA. The content of carbazolylalkyl(meth)acrylate was always lower in copolymer than in the monomer feed and no azeotropic point for all systems was observed. The monomer reactivity ratios of carbazolylalkyl(meth)acrylates (r_1) and MA (r_2) have been determined according to the Kelen Tüdös and Ezrielev procedures [11,12]. By application of the Ezrielev least square method mean square deviations were also calculated. Both results are in good agreement and are presented in Table 4. Reactivity ratios for CEMA-MA and CPMA-MA systems are slightly lower than unity and product r_1r_2, which is a criterion of the tendency of monomers toward alternation or randomess, shows that monomers in both systems have tendency to give random copolymers. The reactivity ratios of CEA ($r_1<1$) and MA ($r_2>1$) indicate that in this copolymerization the incorporation of MA in the copolymer is favored. The product r_1r_2 (=0.49) indicates a tendency towards random copolymerization with some alternation behavior. For the CEMA-MA and CPMA-MA systems the products of reactivity ratios r_1r_2 are higher than for CEA-MA system.

Table 1. Copolymerization of CEMA with MA and copolymer characteristics

Fraction of CEMA in monomer feed (mol %)	Polym. time (min)	Conv. (wt %)	Fraction of CEMA in copolymer (mol %)	$M_n \times 10^4$ (g·mol^{-1})	M_w/M_n	T_g (°C)
0	20	7.34	0	5.8	-	-
10	50	6.89	9.25	4.25	3.14	-
20	70	4.62	15.02	4.3	1.86	-
30	110	5.44	28.34	3.68	2.86	-
40	145	5.08	34.71	3.47	2.19	179
50	180	6.66	45.95	2.68	2.48	172
60	220	5.24	53.79	2.85	3.46	170
70	245	6.13	58.86	2.65	2.16	162
80	280	4.2	65.13	2.52	3.25	155
90	320	7.41	79.77	1.46	3.14	152
100	360	4.9	100	0.88	4.01	133

Table 2. Copolynerization of CPMA with MA and copolymer characteristics

Fraction of CPMA in monomer feed (mol %)	Polym. time (min)	Conv. (wt %)	Fraction of CPMA in copolymer (mol %)	$M_n \times 10^{-4}$ (g·mol^{-1})	M_w/M_n	T_g (°C)
0	20	7.34	0	5.8	-	-
10	60	10.6	9.41	4.68	3.58	-
20	110	9.65	18.31	2.45	3.12	-
40	195	8.14	36.71	3.98	2.56	189
60	270	3.54	55.95	2.83	2.33	182
80	350	4.2	70.77	1.92	2.17	169
90	390	6.91	81.52	1.84	4.05	158
100	420	4.7	100	0.76	2.1	150

As follows from the composition curve (Figure 1) and the product of reactivity ratios, the polymerization will proceed with a higher level of CEMA or CPMA incorporation as compared with CEA. It is typical that methacrylates display a higher reactivity than acrylates, owing to the different resonance reactivity Q and polarity e of the two monomers. Methacrylates generally shows higher values of Q and lower of e, because of the presence of the methyl group at their vinyl ß-carbon atom [13].

Table 3. Copolymerization of CEA with MA and copolymer characteristics

Fraction of CEA in monomer feed (mol %)	Polym. time (min)	Conv. (wt %)	Fraction of CEA in copolymer (mol %)	$M_n\times10^{-4}$ (g·mol^{-1})	M_w/M_n	T_g (°C)
0	20	7.34	0	5.8	-	-
10	60	8.16	2.24	3.2	3.14	-
20	85	7.24	12.02	3.54	3.54	-
30	100	6.31	17.8	2.19	2.96	-
40	120	5.64	22.15	2.54	3.42	-
50	145	5.21	34.23	2.67	2.48	146
60	180	6.36	43.74	2.83	2.91	142
80	225	4.52	62.5	1.96	2.48	116
90	260	7.4	71.6	1.23	1.86	106
100	300	5.2	100	0.26	2.29	81

Table 4. Reactivity Ratios of Carbazolylalkyl(meth)acrylates (r_1) with MA (r_2)

System	Kelen-Tüdös method			Least square method		
	r_1	r_2	$r_1 r_2$	r_1	r_2	$r_1 r_2$
CEMA-MA	0.72	0.98	0.71	0.74±0.09	0.99±0.11	0.73
CPMA-MA	0.88	0.93	0.82	0.89±0.06	0.96±0.07	0.85
CEA-MA	0.29	1.70	0.49	0.27±0.04	1.69±0.21	0.46

All copolymers were soluble in polar aprotonic solvents such as tetrahydrofuran, dimethylformamide, dimethylsulfoxide, which are good solvents for poly(carbazolylalkyl(meth)acrylates). Copolymers were also sligthly soluble in benzene. Copolymers with higher content of MA units (≥70 mol %) were soluble in methanol, ethanol and water. Copolymers with lower MA content were dispersable in water. Methyl ester derivatives of the copolymers (CEMA-MMA, CPMA-MMA, CEA-MMA) were soluble in chlorinated solvents, but solubility in THF was less. They were also insoluble in water and alcohols.

The glass transition temperatures for all carbazolylalkyl(meth)acrylate-MA systems are shown in Tables 1, 2 and 3. T_g values of the prepared copolymers showed approximately linear increase as the content of MA in the copolymer increases. Apparently the increase of the molar fraction of MA in the copolymers enhances intermolecular interactions and thus decrease the mobility of polymer chains. For the carbazolylalkyl(meth)acrylate copolymers with fraction of MA higher than 60 mol % no any T_g for all systems was observed. Thermal analysis of these copolymers confirmed that anhydride formation typical for poly(MA) is taking place above 220 °C [14] and both intermolecular and intramolecular anhydride formation can occur. Poly(MA) does not show any T_g and prediction of the glass transition temperatures as a function of the copolymer composition for carbazolylalkyl(meth)acrylate-MA systems was not possible. The T_g values of copolymers converted into their methyl esters forms (carbazolalkyl(meth)acrylate-MMA) were also established. The monotonic increase of T_g for CEMA-MMA, CPMA-MMA systems and decrease for CEA-MMA system with the increase of carbazolyl content in the copolymer was observed. The different tendencies can be explained taking into account the T_g values of the homopolymers. T_g of poly(CEMA) (133 °C) and poly(CPMA) (150 °C) is higher than that of poly(MMA) (118 °C), while T_g of poly(CEA) (81 °C) is lower than T_g of poly(MMA).

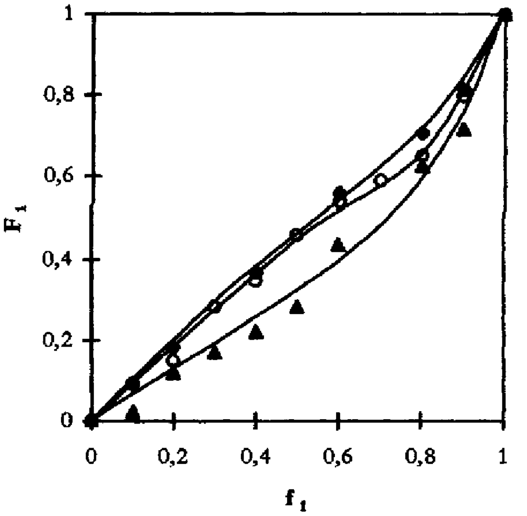

Figure 1. Copolymerization diagrams for CEMA-MA (□), CPMA-MA (□), CEA-MA (□) systems.

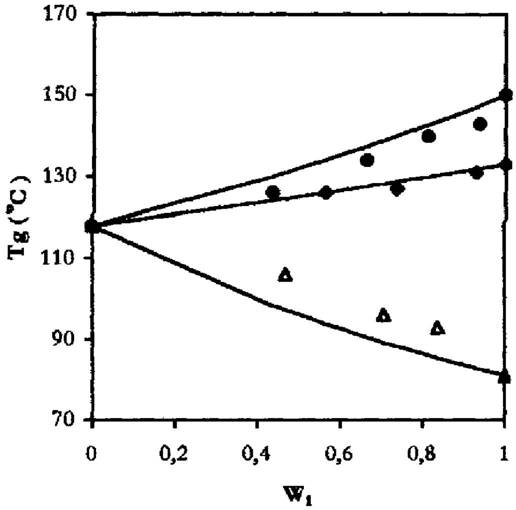

Figure 2. Plot of the glass transition temperatures as a function of the copolymers composition for CEMA-MMA (□), CPMA-MMA (□), CEA-MMA (□). The solid lines represent the values calculated by the Fox equation.

The possible prediction of the glass transition temperatures as a function of the copolymer composition has been considered by the application of several theories. Fox [15] first proposed an additive relation:

$$1/T_g=w_1/T_{g1}+w_2/T_{g2} \qquad (1)$$

where w_2 and w_1 are the MMA and respective comonomer weight fractions in the copolymer; T_{g1} and T_{g2} are the glass transition temperatures of the respective homopolymers. The application of the Eq. (1) for all systems is shown in Figure 2. Di Marzio and Gibbs [16] proposed a simple relation which describes a linear behavior of T_g with copolymer composition:

$$T_g=F_1T_{g1}+F_2T_{g2} \qquad (2)$$

where F_1 (CEMA, CPMA, CEA) and F_2 (MMA) are mole fractions in the copolymer. The application of Eq. (2) for our systems is shown in Figure 3. The expermental T_g values of copolymers do not agree very well with theoretical values predicted by both equations. These theories do not take into account the interactions given by the presence of two different monomeric units. In general, it would be expected that the different nature of the comonomers would generate steric and energetic effects when they are linked together. Furthermore, the heterolinkages would give different contribution to the rotational barrier and free volume than those of the respective homopolymers. In this sense, there are other theories that also consider the sequence distribution in the copolymer.

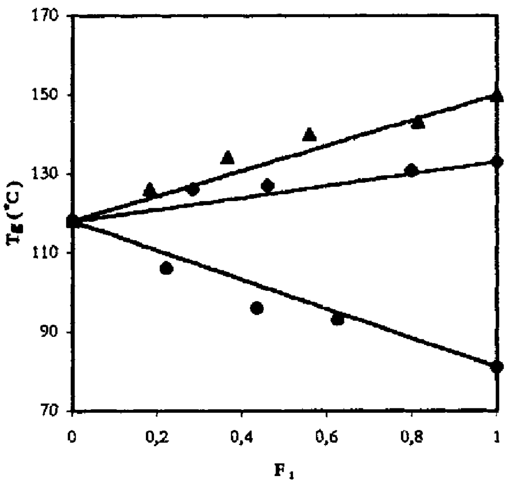

Figure 3. Application of the Di Marzio-Gibbs equation for predicting T_g as a function of the copolymer composition: CEMA-MMA (□), CPMA-MMA (□), CEA-MMA (□), expermental values.

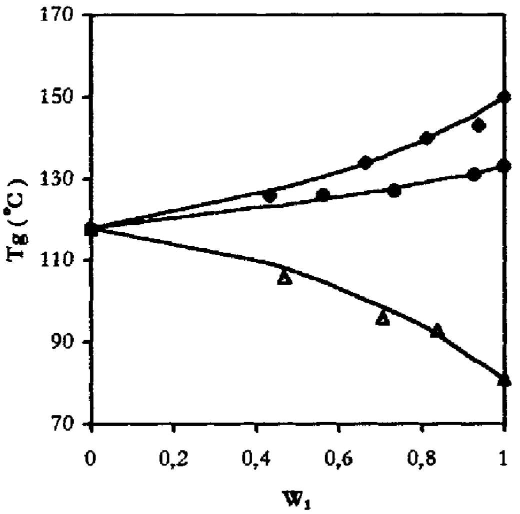

Figure 4. Plot of the glass transition temperatures as a function of the copolymer composition according the Johnston theory: CEMA-MMA (□), CPMA-MMA (□), CEA-MMA (□), expermental values.

One example is the model proposed by Johnston [15], derived from the Fox theory, which assumes that diads formed by equal monomeric units 1-1 or 2-2 have the same interactions as those seen in the respective homopolymers. However, the presence of heterodiads will cause new interactions which could modificate the 1 or 2 monomeric unit contribution to the T_g value. Thus, to predict the T_g more accurately, it is necessary to assign their own T_g values for hetero diads. Assuming that 1-2 and 2-1 sequences have the same T_g, the following equation can be obtained:

$$1/T_g=(P_{11}w_1/T_{g11})+(P_{22}w_2/T_{g22})+(P_{12}w_1+P_{21}w_2)/T_{g12} \qquad (3)$$

where T_{g11} (PCEMA, PCPMA, PCEA) and T_{g22} (PMMA), the glass transition temperatures of both homopolymers, and T_{g12}, that of alternating copolymer. P_{11}, P_{22}, P_{12} and P_{21} are the first-order Markovian transition probabilities of having corresponding linkages in the chain which can be calculated from the reactivity ratios [17]. To apply this theory it is necessary to assign a value to T_{g12}. These values have been obtained from the experimental data of the T_{g11}, T_{g22} and the copolymers T_g prepared at low conversions, using the linearized expression of Eq. (3). The values were: T_{g12}=127.5°C (KEMA-MMA system), T_{g12}=135°C (KPMA-MMA system), T_{g12}=105°C (KEA-MMA system). Figure 4 shows the theoretical dependence of T_g on copolymer composition according to this theory as well as the expermental results obtained. In all systems the T_{g12} is slightly higher that the mean of the respectively homopolymers glass transition temperatures. This fact would indicate the presence of a deviation from the ideal behaviour. According to this, weak attractive interactions between comonomers could be expected. Taking into account the electron-donor behaviour of the poly(carbazolylalkyl(meth)acrylates), these interactions could be generated by electrostatic forces between MMA and respective comonomer. This is more probable in the case of the KEA that is known to form stronger charge transfer complexes with methacrylates than KEMA [18]. As it can be observed the behaviour of the KEMA-MMA system can be predicted adequately by both the Fox and Johnston's theories. It seems that the consideration of the sequence distribution in the copolymer does not improve the results obtained by the application of the Fox's theory. Only weak interactions will exist between both monomers and as both monomers are bulky, the difference between the rotational barrier associated to the heterolinkages or homolinkages could not have a great influence. In relation to the KEA-MMA system, neither of these theories show good agreement with the experimental behaviour. It is probable that as the interactions are not so weak, a more accurate consideration of the heterolinkages contribution could be necessary in order to obtain a better theoretical approximation to the experimental results.

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