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Synthesis and Characterization of Anionic Exchange Resins with a Gradient in Polymer Composition for the PS-co-DVB/PDEAMA-co-DVB System

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Summary

Anionic exchange resins with a gradient in polymer composition were prepared in two stages. After P(S-co-DVB) suspension beads were obtained, N,N diethylaminoethyl methacrylate monomer was let to diffuse into the beads at 25°C, and immediately photopolymerized to fix the gradient polymer composition with high surface concentration of ion exchanger. Chemical composition through the radial position was estimated by means of a mathematical algorithm and using UV spectroscopy. Resin characterization included particle size distribution, "settled" density and total anion exchange capacity, following ASTM D-2187. Values were compared with a porous commercial resin (Amberlite IRA900RF Cl). Since non porous structure with high ion exchange capacity resins were obtained, useful resins for ion exchange with long term stability can be prepared with this methodology.

Introduction

Ion exchange resins to obtain water with low conductivity were first synthesized in 1935 [1]. An advance for resin stability was reached when sulphonic acid groups were incorporated to crosslinked addition polymers [2]. Such methodology allowed the simple preparation of resins varying the ion type, through the modification of a polymer matrix based on polystyrene/divinylbenzene [3, 4]. One more step was the development of resins to exchange specific ions, focusing the researchers on the incorporation of multifunctional ligands into the matrix resin to increase its selectivity, developing chelating resins [5-6]. From there on, research in this area widened with the development of new polymeric matrices [7-10], as well as new and modified polymeric processes to prepare ion exchange resins [11-14].

Among structure variations on this type of polymers, bifunctional resins have been prepared with or without porogen agent [15, 16]. Such family of resins has been recently used to separate selected ions, immobilizing highly selective sorbents over the polymer matrix [17-19]. In addition, the resins have also been obtained by the synthesis of IPNs, where the second network contains two functional groups, looking for cooperative ligands to improve ions separation. However, IPN synthesis involves long diffusion time to reach uniform composition in the polymer bulk or in beads [20]. On the other hand, the application of the gradient composition concept throughout the bulk of an IPN [21-23], allows the possibility to obtain a high surface concentration of the component that diffuses into the matrix, with the advantage of using low diffusion time and low amount of diffusant to reach such high surface concentration. That type of structure has been applied to obtain optical gradients [24], or to gradually release drugs from beads [25], as well as to improve mechanical properties of bulk [21, 22, 26] and emulsion polymers [27, 28].

To obtain ion exchange resins with gradient composition, a monomer carrying specific functional groups (containing initiator) may be let to diffuse at appropriate conditions into the matrix, to obtain a high surface concentration with a relatively small amount of such monomer, even though such concentration decreases rapidly in radial direction. As the second polymerization is carried out immediately after diffusion to fix the high surface concentration of the monomer with functional groups, this method saves the long time required to attain uniform composition of the diffusant, which is needed to prepare IPN ion exchange resins.

In this work, a gradient polymer with tertiary amino groups prepared in two stages is tested as weak basic resin. Chemical composition through the radial direction is evaluated using UV spectroscopy, and considering a mathematical algorithm to convert the PDEAMA average concentration of slices (determined by UV measurements), in a radial profile. To evaluate the potential of this new methodology to prepare ion exchange resins, the exchange capacity of the gradient composition beads is compared with a commercial resin.

Experimental

Materials for polymer synthesis

Industrial grade styrene (S) acquired from "Poliformas de Jalisco" was washed with a 10% NaOH solution, before it was used to prepare the polymer matrix. Reagent grade divinylbenzene (DVB; crosslinking agent) from Aldrich was used as acquired. Industrial grade benzoyl peroxide acquired from AKZO Nobel was recrystallized after dissolution in chloroform, before it was used as initiator. Reagent grade N,N-diethylaminoethyl methacrylate monomer (DEAMA) from Ciba Specialty Chemicals Inc. (coded as AGEFLEX FM2), was used as acquired to prepare the second (anionic) network. In the PDEAMA network formation, Darocur 4265 (50/50 w/w mixture of 2,4,6-trimethylbenzoyl-diphenyl-phosphineoxide and 2-hydroxy-2-methyl-1-phenyl-propan-1-one) from Ciba Specialty Chemicals Inc., was used as acquired to prepare the photoinitiator solution (10 wt % in methanol). To prepare the styrene-divinylbenzene beads, the following industrial grade suspension agents were used as a suspension system: a) aluminum sulfate (from Productos Químicos Monterrey S. A.), b) bentonite (Celite 281, acquired from Celite México), c) poly(vinyl pyrrolidone) (K-90; purchased to Spectrum Chemical Mfg. Corp.), and d) methylhydroxyethyl cellulose (Walocel MKX from Bayer MaterialScience Company).

Polymer matrix preparation

A P(S-co-DVB) matrix was prepared by suspension polymerization in a 1 L glass reactor at 80°C. Polymerization recipe is shown in Table 1. For the recipe, the organic

Table 1. Polymerization recipe used to prepare the poly(styrene-co-divinylbenzene) beads

Organic phase		Aqueous phase	
Substance	Weight (g)	Substance	Weight (g)
Styrene	97	Water	800
Divinylbenzene	3	"Sulfbent" mixture	7.9
Benzoyl Peroxide	1	Poly(vinyl pyrrolidone)	1.7
		Methylhydroxyethyl cellulose	2.4

phase was premixed before it was added to the reactor, and the "sulfbent" mixture was previously prepared as a fine powder that contains aluminum sulfate and bentonite (50/50 w/w). The batch reaction was stopped after 8 hrs. The polymer was washed several times by immersion in distilled water at 60°C. Polymer beads were then sieved, collecting the ones retained over sieves number 20, 30 and 40, to be used for the second network formation.

Weak basic resin preparation

A solution containing DEAMA monomer (96 vol %), divinylbenzene (3 vol %) and the photoinitiator solution (1 vol %), was let to diffuse into a monolayer of P(S-co-DVB) beads at several temperatures, following by gravimetry the swelling behavior as a function of time. After diffusion, beads were surface dried, and immediately allocated to polymerize DEAMA monomer, using four UV 15 watts lamps (General Electric F15T8-BLB) rich in radiation of 366 nm wavelength, during 18 hrs (to assure total conversion). To estimate PDEAMA concentration through the bead radius, beads without divinylbenzene for DEAMA polymerization were also prepared, following the above procedure.

Radial composition profile estimation

To estimate the radial composition profile of functionalized beads, two sets of 20 similar diameter beads (d_b), were taken at random to be microtomed in slices. As it is shown in Figure 1, eleven slices with the same thickness ($d_b/21$) were sequentially cut in planes located in orthogonal position with respect to the cylindrical z coordinate, beginning at the bead surface; due to the difficulty to obtain the predefined thickness, the first slice of each bead was discarded. For each set of beads, the correspondent numbered slices were collected separately to extract their PDEAMA content, using water stirred and heated at 50°C during 96 hrs. The PDEAMA concentrations of such aqueous solutions were determined by using UV analysis (Genesys 10), considering the absorbance at 199 nm and the Beer's law ($\varepsilon_{199\ \mathrm{nm}} = 2 \times 10^3$ L/mol·cm; calculated by linear regression -R > 0.9998-, considering DEAMA molar mass and 8 experimental points); for the gravimetric measurements a Sartorius balance (BP211D) with precision of 0.01 mg was used. From each experimental concentration value, the average PDEAMA concentration of the respective numbered slice was evaluated. Since the average PDEAMA concentration in every slice depends on the radial composition profile developed in the bead, the set of concentration values (one for each slice), can be used to estimate such profile. To correlate the PDEAMA concentration (α) with its radial position (r), equation 1 is proposed:

$$\alpha = a\left(\frac{1}{r} - \frac{1}{r_o}\right)^2 + b\left(\frac{1}{r} - \frac{1}{r_o}\right) \qquad (1)$$

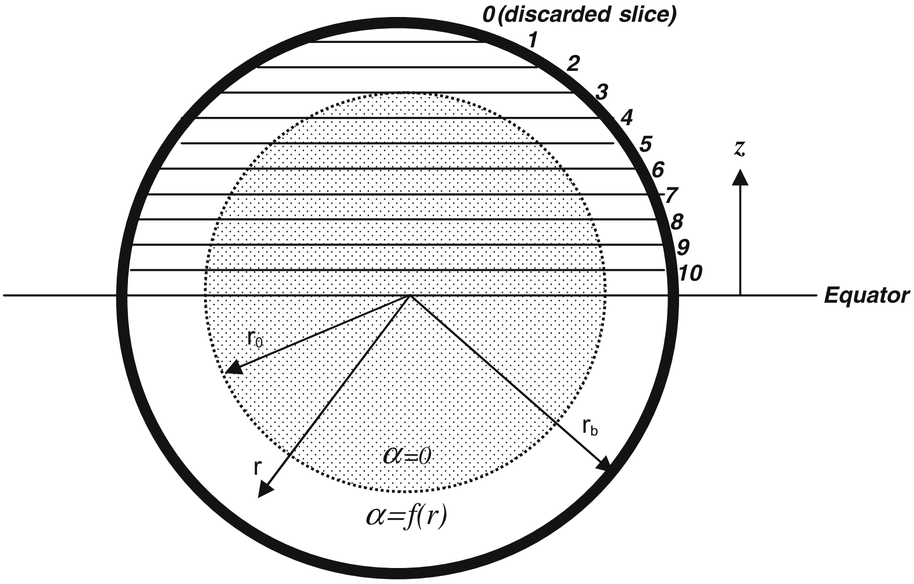

Figure 1. Schematic projection of a PS-co-DVB/PDEAMA-co-DVB bead in the *z-x* Cartesian plane.

Such equation applies only for the bead sector where the PDEAMA is present (outer ring in Figure 1; $r > r_o$); consequently, it was considered that if $r \leq r_o$ (inner circle in Figure 1) then $\alpha=0$. In addition, since one of the equation parameters is defined by the mass balance in the bead, the other two can be iteratively modified to obtain the best fit profile. Therefore, using a trial and error methodology, such parameters were modified to create iterative profiles that show the maximum PDEAMA concentration value at the particle surface ($r = r_b$). The respective iterative profile was used to calculate the PDEAMA average concentrations in the different slices, and such calculated values were compared with the correspondent experimental ones, choosing as the best fit profile the one that showed the minimum average quadratic deviation between the calculated and the experimental concentrations.

Microscopic characterization

Scanning Electron Microscopy (SEM; Jeol JSM 5400 LV) was used to observe the "equatorial" surface of synthesized beads that were microtomed (Reichert Austria Nr. 366999) and stained with a 1 wt % OsO_4 aqueous solution.

ASTM characterization of resins

Weak basic polymer beads synthesized in this work and one supplied by Rohm and Haas, selected as a weak resin that resists high temperatures (Amberlite IRA900RF Cl) were characterized following ASTM D-2187. The characterization included: a) "settled" density (test C), b) particle size distribution (test D) and, c) total anion-exchange capacity (test M).

Results

In Figure 2, the resin swelling behavior at various temperatures is presented. There, it can be observed that DEAMA diffusion is slow up to 3600 s for the 5-15°C temperature range; this phenomenon is mainly due to a high mass transfer barrier. At 20°C, a noticeable change in slope comparing to the former curves starts at approximately 1200 s. Swelling curve at 25°C shows an initial slope that is higher than the ones for curves at lower temperatures, allowing a 50 wt % uptake in approximately 30 minutes. In the diffusion carried out at 30°C, even at short times, a high DEAMA uptake was reached, denoting a considerable change in diffusion behavior [29]. Such behavior would difficult the beads preparation with a pre-selected PDEAMA content. For that reason, to prepare in a reasonable way batches of weak basic resins with various PDEAMA average concentrations, trying to attain considerable monomer penetration (e.g. between 10 and 40 wt %) with a concentration gradient in radial direction, the temperature of 25°C and the following diffusion times were selected: 10 (resin A), 20 (resin B), and 30 minutes (resin C).

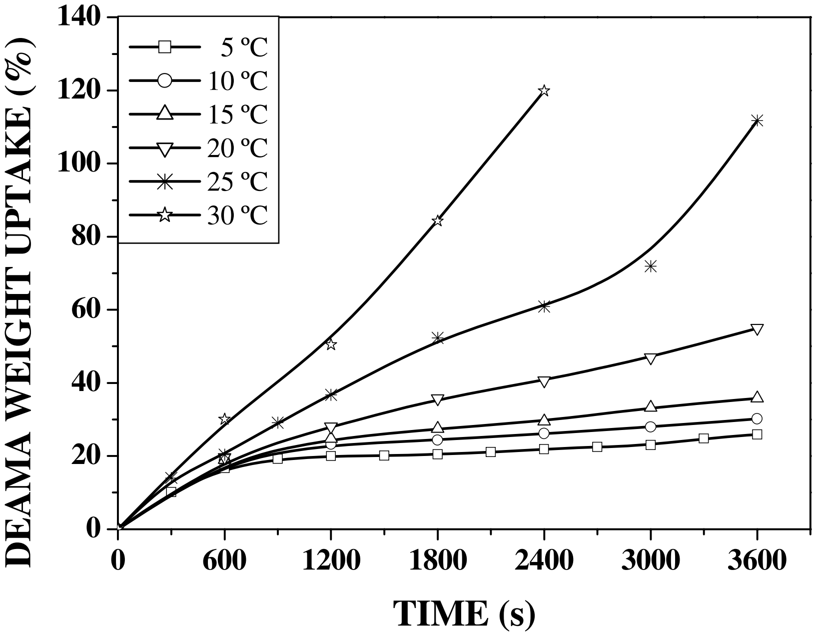

Figure 2. Uptake of solution with DEAMA by crosslinked PS as a function of time of immersion, at different temperatures.

In Figure 3, the experimental average PDEAMA concentrations of the numbered slices (series I and II), and the correspondent ones calculated considering the concentration profiles numerically estimated for the beads, are presented. There, for the three resins, it can be noticed that the differences between the equivalent experimental values of series I and II, as well as the differences between the correspondent experimental and estimated concentration values, can be neglected. Therefore, it can be established that the selected quadratic profiles adequately represent the experimental concentration data.

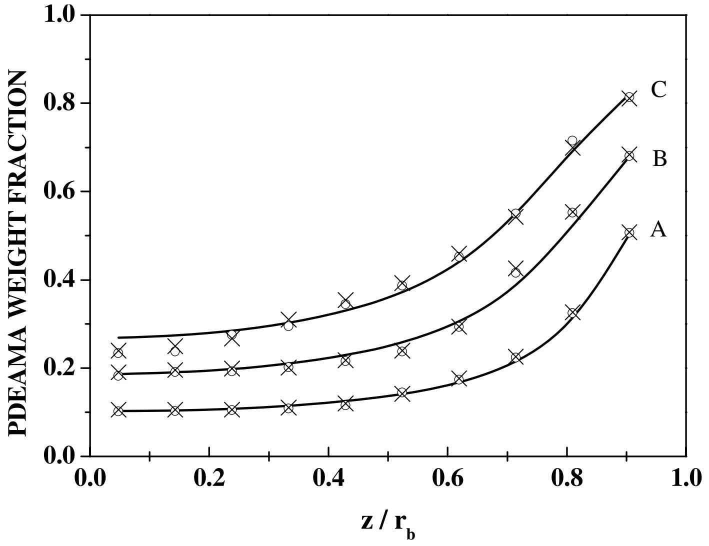

Figure 3. Experimental (x, o) and estimated (—) values of PDEAMA weight fraction for bead slices, as a function of normalized z coordinate.

The numerically estimated radial concentration profiles and SEM micrographs of beads prepared using different DEAMA diffusion times (resins A, B, and C), are shown in Figure 4. The normalized penetration depths ($1\text{-}r_o/r_b$ values) for the different resins presented in Figure 4 (a-c) are the following: A: 0.11; B: 0.22; C: 0.27. As it could be expected, such values increase in a non-linear way as the diffusion time increases [23], showing the three resins a low penetration value; that is, in all cases, the PDEAMA present in the beads is located near to the surface. In such Figure, it can also be observed that the highest PDEAMA surface concentration (75 wt %) was obtained with resin C, which assures a high surface concentration of active groups. A qualitative confirmation of DEAMA radial penetration as a function of diffusion time can be observed in the micrographs of Figure 4 (d-f). As the amine groups of PDEAMA are stained with OsO_4 [30], a diffuse dark ring including the bead surface can be noticed in resin A (Figure 4d), while in resins B (Figure 4e) and C (Figure 4f) a more uniform ring can be observed. It is important to notice that, as the OsO_4 staining capability is reduced in the section where PDEAMA concentration is low, the observed penetration depth in SEM micrographs is smaller than the one numerically estimated.

Table 2 shows the PDEAMA average concentration obtained from UV measurements, the "settled" density values, and the particle size distribution for the tested resins. A comparison among the values corresponding to synthesized beads shows that as the diffusion time increases, the PDEAMA content increases, and for such reason, a higher amount of water can be incorporated in the resin, decreasing the value of "settled" density (ρ_s); that happens because the density of dry polymer is higher than water density. It can also be noticed that "settled" density of commercial resin is higher than the one obtained for synthesized resins; that represents a potential economic advantage of the resin here developed, because this type of product is commercialized on a weight basis. For particle size distribution, a great similarity among resins can be seen in Table 2; that is an important requirement to measure ion

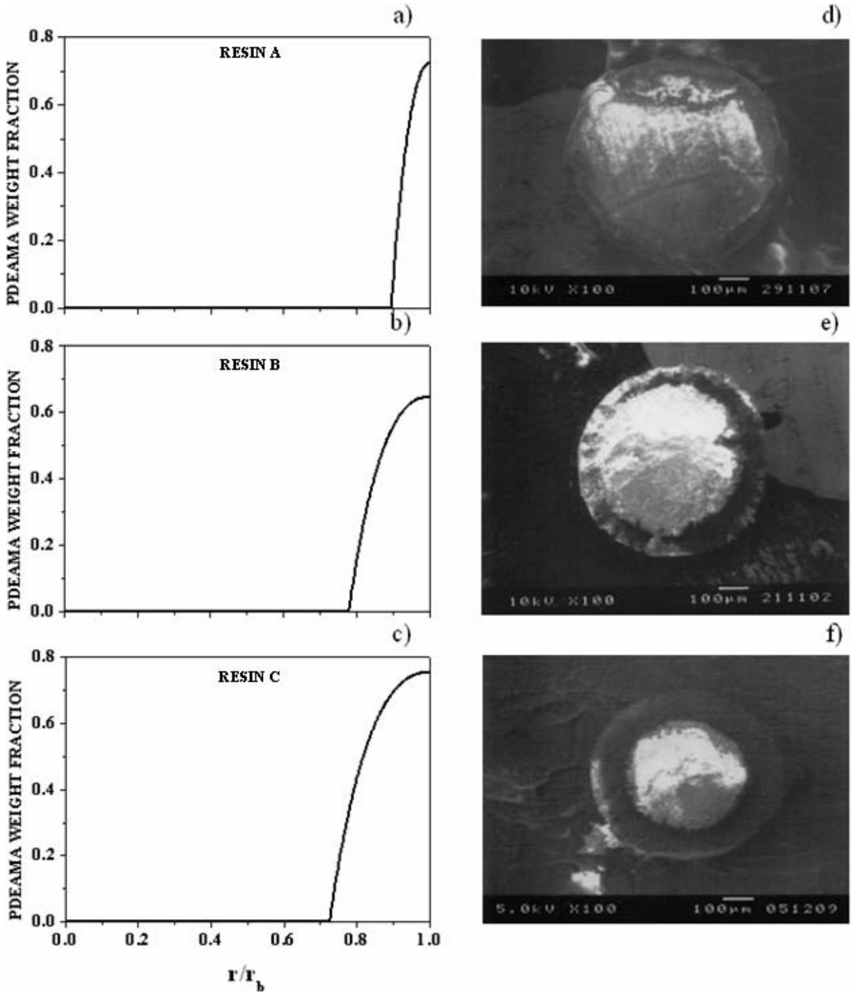

Figure 4. Numerically estimated PDEAMA weight fraction as a function of normalized bead radius (a-c), and the correspondent SEM micrographs for synthesized resins (d-f); for resins code, see Table 2.

Table 2. PDEAMA average concentration, "settled" density and particle size distribution of synthesized and commercial anionic exchange resins

Resin code	PDEAMA average concentration (wt %)	"Settled" density (g/mL)	Sieve number	16	20	30	40	50
			Pore size (µm)	1180	850	600	425	300
A	15	0.68	Retained over sieve (vol %)	1	8	70	20	1
B	26	0.66		1	4	76	18	1
C	36	0.65		2	8	72	18	0
Amberlite IRA900RF Cl		0.71		0	2	83	13	2

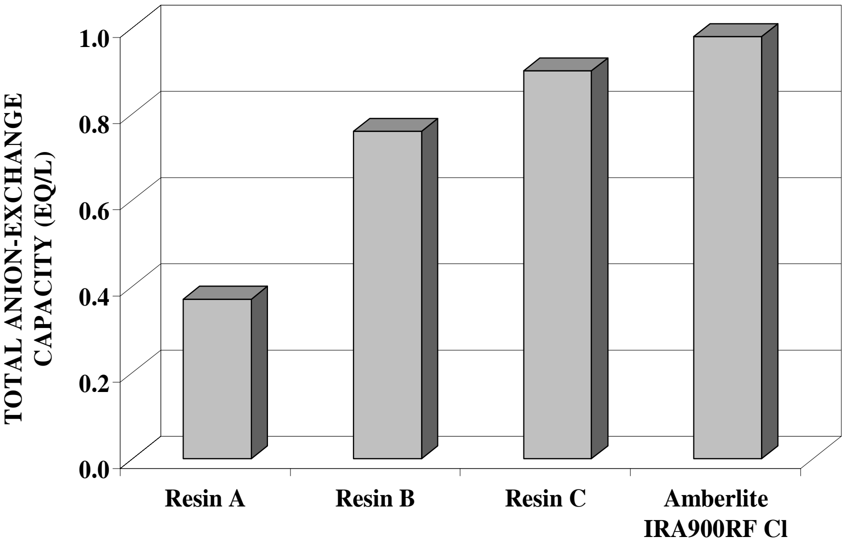

Figure 5. Total anion-exchange capacity of resins A, B, C and, Amberlite IRA900RF Cl; for resins code, see Table 2.

exchange in similar conditions. For all cases, at least 90 vol % of the beads was collected in sieves number 30 and 40, being the number 30 the dominating one.

To analyze in Figure 5 the effect of diffusion time on exchange behavior, it can be noticed that the resin B exchange capacity is notoriously higher than the one of resin A, and the resin C shows, with respect to resin B, only a slight additional increment in its ion exchange capacity. Moreover, a comparison among the total anion exchange capacity values for resins B, C and, Amberlite IRA900RF Cl shows that, it is possible to obtain high exchange values without porous formation. To reach such high values, the high PDEAMA surface concentration in beads plays an important role. In addition, DEAMA penetration to a certain extent, assures the exchange in layers beyond the surface. The absence of porogen agent (along with inclusion of crosslinking agent) in synthesized beads, avoids porous formation, promoting long term stability for such resins. That is important because porous or macroporous commercial resins have a disintegration problem in the long term, by the excess of water retention in beads.

Conclusions

The application of the gradient concept in polymeric materials can be used to synthesize ion exchange resins, by using a monomer carrying specific functional groups, to prepare the second network. A high bead surface concentration of the ion exchanger, complemented with radial penetration to a certain extent, allows the possibility to obtain high ion exchange capacity, avoiding the use of a porogen agent, as it is commonly used in commercial resins. With this methodology, long term stability resins for ion exchange may be obtained.

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References

1. Adams BA, Holmes EL (1935) J Soc Chem Ind 54:1T
2. D'Alelio (1944) U S Patent Office 2,366,007
3. Bodamer GW (1952) U S Patent Office 2,597,438
4. Boyd GE, Soldano BA (1954) J Am Chem Soc 75:6091
5. Helfferich F (1962) J Am Chem Soc 84:3237
6. Moyers EM, Fritz JS (1976) Anal Chem 48:1117
7. Coutinho FMB, Siqueira MIN, Barbosa CR (1990) Eur Polym J 26:1189
8. Iayadene F, Guettaf H, Bencheinkh Z, Saggou A, Rabia I (1998) Eur Polym J 34:219
9. Kolarz BN, Jermakowicz-Bartkowiak D, Trochimczuk A (1998) Eur Polym J 34:1191
10. Alexandratos SD, Zhu X (2003) Macromolecules 36:3436
11. Chong BP (1980) U.S. Patent Office 4,191,712
12. Alexandratos SD, Grady CE, Crick DW (1991) Macromolecules 24:6365
13. Jégat C, Bois A, Camps M (2001) J Polym Sci 39:201
14. Li F, Larock RC (2003) Biomacromolecules 4:1018
15. Alexandratos SD, Strand MA, Quillen AR, Walder AJ, (1985) Macromolecules 18:829
16. Alexandratos SD, Wilson DL, (1986) Macromolecules 19:280
17. Dambies L, Salinaro R, Alexandratos SD (2004) Environ Sci Technol 38:6139
18. Zhu X, Alexandratos SD (2005) Ind Eng Chem Res 44:7490
19. Zhu X, Alexandratos SD (2005) Ind Eng Chem Res 44:8605
20. Alexandratos SD, Grady CE, Crick DW, Beauvais R (1994) Bifunctional Interpenetrating Polymer Networks. In: Klempner D, Sperling LH, Utracki LA (ed) Interpenetrating Polymer Networks. American Chemical Society, Washington, D C. (Adv Chem Ser. vol 239, pp 197-203)
21. Akovali G, Biliyar K, Shen M (1976) J Appl Polym Sci 20:2419
22. Jasso CF, Hong D, Shen M (1979) Stress-strain behavior of PMMA/CIEA gradient polymers. In: Cooper SL, Estes GM (eds) Multiphase Polymers. American Chemical Society, Washington, D C. (Adv Chem Ser. vol. 176, pp 443-453)
23. Jasso CF, Valdéz J, Pérez JH, Laguna O (2001) J Appl Polym Sci 80:1343
24. Krivchenko EI, Matveenko RV, Phvlova VN, Budtov VP, Gandelisaman MI, Egorova EI, Ginsburg LI (1988) Plasticheskie Massy 4:26
25. Mueller KF, Heiber SJ (1982) J Appl Polym Sci 27:4043
26. Jasso CF, Martínez JJ, Mendizábal E, Laguna O (1995) J Appl Polym Sci 58:2207
27. Jasso-Gastinel CF, Reyes-González I, López-Ureta LC, González-Ortiz LJ, Manero-Brito O (2006) Inter J Polym Anal Charact 11:383
28. Jasso-Gastinel CF, López-Ureta LC, González-Ortiz LJ, Reyes-González I, López-Dellamary-T FA, Manero-Brito O (2006) J Appl Polym Sci 103:3964
29. Alfrey T, Ournee EF, Lloyd WG (1966) J Polym Sci 12:249
30. Sawyer LC, Grubb DT (1996) Polymer Microscopy. Chapman & Hall, London