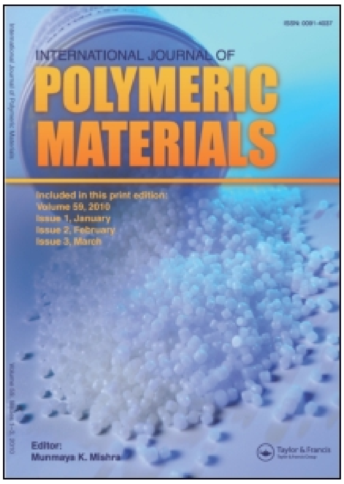

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

On the structure and physicochemical properties of acrylic compounds

R. Vera-Graziano[a]; J. Palacios-Aiquisira[a]; A. Martínez-Richa[b]; F. Barceló[c]; T. Halachev[d]; V. M. Castaño[d]
[a] Facultad de Química, UNAM, Mexico City, D.F., Mexico [b] Facultad de Química, Universidad de Guanajuato, Guanajuato, Mexico [c] Facultad de Odontologia, UNAM, Mexico City, D.F., Mexico [d] Centro de Física Aplicada y Tecnologia Avanzada, UNAM, Querétaro, Qro., Mexico

To cite this Article Vera-Graziano, R. , Palacios-Aiquisira, J. , Martínez-Richa, A. , Barceló, F. , Halachev, T. and Castaño, V. M.(2003) 'On the structure and physicochemical properties of acrylic compounds', International Journal of Polymeric Materials, 52: 2, 85 — 95

To link to this Article: DOI: 10.1080/714975922

URL: http://dx.doi.org/10.1080/714975922

International Journal of Polymeric Materials, 52:85–95, 2003

0091-4037/03 $12.00 + .00
DOI: 10.1080/00914030390119253

ON THE STRUCTURE AND PHYSICOCHEMICAL PROPERTIES OF ACRYLIC COMPOUNDS

R. Vera-Graziano and J. Palacios-Alquisira
Facultad de Química, UNAM, Cd. Universitaria, Mexico City,
D.F., Mexico

A. Martínez-Richa
Facultad de Química, Universidad de Guanajuato,
Guanajuato, Guanajuato, Mexico

F. Barceló
Facultad de Odontologia, UNAM, Cd. Universitaria,
Mexico City, D.F., Mexico

T. Halachev and V. M. Castaño
Centro de Física Aplicada y Tecnologia Avanzada, UNAM,
A.P. 1-1010, Querétaro, Qro. 76000, Mexico

The chemical structure of four acrylic polymers (P1-P4) used for producing dental cements was studied by FTIR, ^{1}H and ^{13}C NMR, using polyacrylic acid (PAA) as a reference compound. Both, P1 and P2 are PAA polymers containing low concentration (<5 wt.%) of a carboxylic precursor. Besides, sample P2 contains also traces of the monomer (acrylic acid). Sample P3 is a random co-polymer (acrylic acid/methyl acrylate) in ratio 2 : 1, whereas sample P4 is an oligomer of 2-hydroxyethylacrylate. Three thermodynamic models were applied to the study of the perturbed and non-perturbed molecular parameters of the polymers using viscosimetric and chromatographic determination of their molecular weights. The best fitting of the experimental results was obtained by the Flory-Fox-Schaefgen model. In perturbed conditions samples P1 and P2 show the presence of flexible chains, while samples P3 and P4 contain semi-rigid chains. The lyophilization of the polymers at 50° C resulted in the

---

Received 19 September 2000; in final form 25 September 2000.

The authors wish to express their gratitude to the following students for their valuable collaboration: Mariana Latorre García, Patricia F. Miyki Ishihara, Luz Ma. Lazo Jimenez, Carlos Alvarez. Gayosso, Dante S. Díaz Suárez, Arturo Bolaños Angeles, and Jorge Guerro Ibarra. We also thank the staff members Araceli Ordoñez Medrano, Miguel A. Canseco Martínez, and Juan M. García León. Financial support for this project was provided by DGAPA, UNAM.

Address correspondence to V. M. Castaño, Centro de Física Aplicada y Tecnologia Avanzada, UNAM, A.P. 1-1010, Querétaro, Qro. 76000, Mexico. E-mail: meneses@servidor.unam.mx

formation of hydrolysable cyclic anhydrides (soluble fraction) and in chemical cross-linking (insoluble fraction).

Keywords: dental cements, acrylates, chemical structure, molecular parameters, acrylic anhydrides

INTRODUCTION

Bone and dental cements formed by acrylic esters and/or reinforced with minerals and/or polymers have found widespread applications in medicine as prosthesis adhesives, seals and reconstructive materials in bones and teeth. In general, these materials are applied upon mixing two phases, namely: a liquid phase containing the dissolved polymer and a solid phase containing the reinforcements and the chemical reaction promoters. Upon application, the two phases are mixed together to form a fluid of adequate viscosity, which is solidified "*in situ*" by a chemical reaction in the presence of chemical or photochemical promoters. Chemical promoters are used in different surgical applications such as deep dental restorations and bone implants due to the practical impossibility to start the chemical reaction by a photochemical initiator [1, 2].

Bone and dental cements should meet very strict specifications imposed by professional international associations such as The World Health Organization, the ADA, etc. Besides the chemical, physical, biological and some times aesthetical characteristics, other requirements should also be fulfilled. The liquid phase must possess adequate initial viscosity and long term stability during storage. The phases should be easily mixed and should have adequate reaction time in specific applications. Once applied, the cement should show adequate mechanical performance, adhesion to the bone tissue and hydrolysis stability [1 – 3].

Acrylic polymers have been widely used in bone and dental cements due to their adequate characteristics. However, upon application some problems such as dimensional stability and interfacial cracking have been observed [3]. Therefore, profound knowledge of their molecular parameters and interfacial interactions is necessary to avoid these problems. Many acrylic polymers behave as polyelectrolytes in aqueous solutions. This results in the formation of aggregates, which induce changes in the conformation and properties of the cements. The mechanisms of the above phenomena are not well understood yet [4, 5].

It is well known that the mechanical, optical, thermal, electrical and rheological properties of the polymers can be estimated on the basis of their molecular weight and from the macromolecular conformation. Keeping in mind the above considerations, in the present paper we report the results on the study of the chemical structure, molecular parameters and dimensions of four acrylic polymers. Polyacrylic acid, PAA, was used as a model compound because its chemical structure and molecular parameters at normal and perturbed conditions are well known [6, 7].

THEORETICAL BACKGROUND

The viscosimetric molecular weight, M_v, can be obtained from Mark-Houwink equation:

$$[\eta] = K(M_v)^a, \tag{1}$$

where $[\eta]$ is the intrinsic viscosity, K and a are parameters of a polymer-solvent pair [8]. The value of a varies from 0.5 in a poor solvent at temperature θ up to 0.8 in a thermodynamically good solvent. The theoretical details have been published elsewhere [9–11].

In the present study we used three thermodynamic models, which predict, in terms of the intrinsic viscosity, the behavior of diluted solutions of polymer of moderate molecular weight. The following expressions were used:

- the Flory-Fox-Schaefgen model, (FFS), [12]:

$$[\eta^{2/3}]/M_v^{1/3} = K_\theta^{2/3} + 0.858\, K_\theta^{2/3}\Phi_0 B M_v/[\eta], \tag{2}$$

- the Stockmayer-Fixman model, (SF), [13]:

$$[\eta^2]/M_v^{1/2} = K_\theta + 0.51\ \Phi_0 B M_v^{1/2}, \tag{3}$$

and the Berry model, (Be), [14]:

$$[\eta^{1/2}]/M_v^{1/4} = K_\theta^{1/2} + 0.42 K_\theta^{1/2}\Phi_0 B M_v/[\eta]. \tag{4}$$

The semi-empirical equation of Krigbaum, (Kr), [15] was used to evaluate the second virial coefficient, A_2:

$$[\eta] = [\eta]_\theta + 0.005 A_2 M_v. \tag{5}$$

The quantities $\langle R_\theta^2\rangle$, length of the statistical element, b, and the coefficient of chain stiffness, σ, can be evaluated using the following equations:

$$b = (K_\theta/\Phi)^{1/3}(m_0)^{1/2}, \tag{6}$$

$$\langle R_\theta^2\rangle = M_v A^2, \tag{7}$$

$$\sigma = (\langle R_\theta^2\rangle/M_v)^{1/2}/(\langle R_{of}^2\rangle/M_v)^{1/2}, \tag{8}$$

$$(\langle R_{of}^2\rangle/M_v)^{1/2} = 0.218(m_0)^{1/2}, \tag{9}$$

where m_0 is the molecular weight of the basic repeating unit and $\langle R_{of}^2 \rangle$ is the root mean square end to end distance of the freely rotating chain [16].

The effect of the molecular weight on the molecular parameters has been carefully examined [9, 11]. The solutions of PAA in anhydrous 1,4-dioxane, which is considered a poor solvent, are not ionic. The value of the K_θ constant in these solutions at 30°C is equal to 8.5×10^{-4} dL/g. However, the same solutions in 1,4-dioxane containing 2% to 4% of water manifest some ionic properties, which results in an increase of the stiffness of the chains due to inter-chain interactions. The value of a at this temperature is 0.6 and that of K_θ is $6.6\ (\pm 2) \times 10^{-4}$ dL/g [7, 9, 17].

The evaluation of the molecular weight by GPC was based on the method of universal calibration. The dimensions of the dissolved macromolecules are proportional to their hydrodynamic volume, e.g., to $[\eta][M_v]$. After some algebra with the equations involved, one obtains [18, 19]:

$$[\eta]M_v = \Phi \langle R_0^2 \rangle^{3/2} \alpha^3. \tag{10}$$

EXPERIMENTAL

Materials

Model compounds having different molecular weights were prepared from aqueous solutions of PAA (Aldrich, reactive grade) via free radical polymerization. Ammonium persulfate was used as an initiator and 2-propanol as a chain transfer agent [20–22]. The polymerizations were carried out in a 316 stainless steel reactor (Parr Ins. Co.), equipped with a reflux column and automatic temperature and stirring controllers. The synthesized PAA were purified by precipitation, followed by dissolving in 1,4-dioxane. The PAA has an average content of 88 vol.% of acrylic acid, as determined by titration with NaOH. The dental commercial polymers (P1–P4) were supplied by the Faculty of Dentistry of UNAM, Mexico and their chemical structure was studied by comparing it to that of the reference compounds. 2-hydroxyethylmethacrylate (HEMA), methyl acrylate (MA), methacrylic acid, +(−) tartaric acid, itaconic acid and maleic acid (Aldrich, all reagent grade) were used as model compounds.

CHARACTERIZATION

FTIR and NMR

The chemical structure of the samples was studied by FTIR and NMR (^{1}H and ^{13}C). The FTIR spectra were recorded on a Nicolet 510P spectrometer using CsI cells with reference to air. The NMIR spectra of the solutions were recorded on a Varian Gemini 200 spectrometer. The solid state NMR spectra were recorded on a Varian Unity Plus 300 equipment, operated at 75.74 MHz for ^{13}C. The CP-MAS spectra were obtained at Hartmann-Hann conditions with a contact time of 2 ms, repetition time of 4s and rotor speed rate of 4.5 to 5 kHz. The elimination of side bands was carried out by means of TOSS sequence. The chemical shifts in solid state are reported relative to the right hand peak of adamantane at 29.5 ppm. The 2D spectra were obtained by using pulse sequences for HETCOR and COSY.

Solubility Measurements

In order to avoid thermal decomposition the polymers were dried by lyophilization at 50°C and 0.08 mbar in a Hectosic Co. equipment having a rotational RZ2 pump. The weight of the solid residue of each dried polymer was measured and then the samples were redissolved in deionized water and in 1,4-dioxane (HPLC grade) to determine their solubility in each one of the solvents.

GPC and Intrinsic Viscosity

The average molecular weight and the mass distribution were determined using a Waters GPC-150/C chromatograph, having a series of μ-Bondagel (Millipore) separation columns in the interval from 500D to 2×10^6D. All solutions were previously filtered through 0.22 μm PTFE filters (Cole Palmer). The universal calibration method based on the above equations was applied to calibrate the GPC equipment using ten standards of previously degassed and filtered mono-dispersed polystyrenes (molecular weight between 500 and 500000) dissolved in 1,4-dioxane. The average molecular weights reported here are equivalent to the radius of gyration of the polystyrene standards. This method has been successfully applied to solutions of PAA with random position of the side groups and to their homologues [7]. The viscosimetry measurement of the polymer solutions were carried out in a Ubbelohde capillary viscometer following the ASTM D2857-87 standard at perturbed and non-perturbed conditions. The solutions were filtered and special measures were taken to assure flow times between 2 and 3 min.

RESULTS AND DISCUSSION

Chemical Composition and Structure

The synthesized PAA and samples P1 and P2 show ^1H-NMR peak patterns typical for PAA with random distribution of the side groups. The spectra indicate the presence of three CH_2 peaks at 1.7, 1.88 and 2.05 ppm. Also, a peak at 2.55 ppm, assigned to a CH group is observed. The ^{13}C-NMR spectrum in D_2O solution contains the peak of CH at 44.4 ppm and a peak at 181.5 ppm assigned to the CO group of the acid. An additional peak at 2.32 ppm is observed in the ^{1}H-NMR spectrum of sample P1, which is attributed to the presence of a small amount of the polymer precursor. The ^{1}H-NMR spectrum of sample P2 contains two additional small peaks at 5.7 and 6.2 ppm due to the presence of residual monomer (acrylic acid) [23]. The ^{1}H and ^{13}C-NMR spectra of sample P3 recorded in D_2O indicate that the sample is a co-polymer – PAA/PMA (acrylic acid/methyl acrylate). The identification of the copolymer was additionally confirmed by ^{1}H-^{13}C correlated spectrum (HETCOR). The methoxyl group appears at 4.6–4.7 ppm in the ^{1}H-NMR spectrum and at 74.8 ppm in the ^{13}C spectrum. The ester and acid carbonyl groups appear at 177.5 and 181.7 ppm, respectively. The AA/MA ratio (2 : 1) was calculated by integration of the peak area of the ^{13}C-NMR spectrum and using a sequence for ^{1}H decoupling and NOE suppression. Sample P4 is an oligomer of HEMA. The peak of the CH_3 group appears at 2.0 ppm in the ^{1}H-NMR spectrum and at 25.2 ppm in the ^{13}C-NMR spectrum. The CH_2OH group is observed at 3.9 ppm in the ^{1}H-NMR spectrum and at 70.3 and 74.1 ppm in ^{13}C-NMR, while the ^{t}HC of the double bond group appears at 5.79 ppm in the ^{1}H-NMR and at 134.7 ppm in ^{13}C-NMR. The ^{c}HC group is registered at 5.86 ppm in the ^{1}H-NMR spectrum and at 143.5 ppm in ^{13}C-NMR, whereas the carbonyl group is observed at 177.1 ppm in the ^{13}C-NMR.

The FTIR spectra of samples P1 and P2 contain the typical peak patterns of PAA [24]. The FTIR spectra of samples P3 and P4 were compared to the spectra of poly(methyl acrylate) (PMA) and of HEMA in the Aldrich and Nicolet libraries. The peak patterns of samples P3 and P4 coincided with these of the library compounds.

All acrylic polymers showed an initial 99% solubility in water. After lyophilization the polymers manifested different degrees of solubility both in water and in 1,4-dioxane. The insoluble fractions could not be redissolved in water even after 15 days in an ultra-sonic bath, which strongly indicates that chemical cross-linking has occurred in the samples.

All reports [11] on the thermal behavior of PAA and of PMA conclude that above 200°C intermolecular anhydrides are formed, while at temperatures below 150°C the formation of cyclic intramolecular anhydrides is favored. This is evidenced by the presence of a band in the FTIR spectra at 1750 cm^{-1} characteristic of carboxylic anhydrides and by a peak at 168.5 ppm for PAA and at 172 ppm for PMA in the ^{13}C-NMR spectra [25, 26]. Therefore, the lyophilization of the acrylic acid and of PAA/PMA copolymers favors the formation of intra- and intermolecular anhydride bonds.

All our samples were redissolved in water after lyophilization and the soluble and insoluble fractions were analyzed by ^{13}C-NMR. Both fractions of samples PAA, P1 and P2 show a peak at 168 – 170 ppm, corresponding to the carbonyl group of the carboxylic anhydride. The lyophilization of the co-polymer P3 gave 11 wt.% of an insoluble fraction, which indicates that chemical cross-linking took place resulting in the formation of intermolecular anhydrides moieties. It is likely that cyclic carboxylic anhydrides were formed between repetitive adjacent units of the acrylic acid and of the methyl acrylate, accompanied by the corresponding loss of methanol.

The solid state ^{13}C CP-MAS NMR spectrum of the soluble fraction of sample P3 contains a peak at 171.9 ppm, which corresponds to intramolecular cyclic carboxyl anhydrides. The ester and acid carbonyl groups are observed at 176.6 and at 180.0 ppm, respectively. Besides, two types of methoxyl groups are registered at 72.3 and at 74.6 ppm, which suggests the presence of two different surroundings. These results indicate the formation of intramolecular cyclic carboxylic anhydrides in the soluble fractions, which probably involve adjacent repeating units. Chemical cross-linking in the insoluble fractions also results in the formation of anhydrides.

It has been reported [27] that gels are formed after storage from 3 to 6 months of 40 – 50% aqueous solutions of acrylic dental polymers. It has been suggested that the formation of these gels is due to the existence of hydrogen bonding. The aqueous solutions of PAA/PMA co-polymers are more stable and resistant to gelation as compared to the solutions of PAA with the same concentrations. However, the former manifest a higher viscosity. The viscosity increases due to the chain rigidity caused by the presence of the methyl group in the chain. This rigidity impedes the formation of hydrogen bond bridges and decreases gelation. The formation of cyclic anhydrides also results in the above mentioned effects.

The lyophilization of sample P4 resulted in the formation of a water insoluble fraction (19%), which is again attributed to chemical cross-linking. These reactions of the HEMA oligomer are presently being studied by FTIR and NMR.

Molecular Parameters

The molecular weights obtained by GPC are compared to the values obtained by $[\eta]$-Table 1 and Table 2. Correction factors were used for the polydispersity in order to adjust the experimental results at perturbed and non-perturbed conditions [17]. The values of α for the PAA sample were calculated using the values of $[\eta]_0$ in 1,4-dioxane at 30°C and of $[\eta]$ in 0.1 M NaBr at 25°C. The a and K values for PAA/PMA were evaluated at 30°C in 1,4-dioxane (HPLC grade) assuming that the copolymer is PAA and that it has 66% of repeating units of acrylic acid. Using these values we calculated the intrinsic viscosities from the M_w values as obtained by GPC. The values

TABLE 1 Molecular weight distribution as evaluated by GPC

Sample and polymer composition	M_n	M_w	M_z	M_w/M_n
PAA-1, PAA	5,920	56,800	219,890	9.6
PAA-2, PAA	3,990	44,630	137,360	11.1
P1, PAA	5,331	26,560	58,890	5.0
P2, PAA	3,530	19,900	41,640	5.6
P3, P(AA/MA):				
1st peak	4,740	12,400	25,540	2.6
2nd peak	31	430	910	14.0
P4, P(HEMA)				
1st peak	1,470	4,650	9,820	3.1
2nd peak	45	210	360	4.8

TABLE 2 Intrinsic viscosities, α and radius of gyration values

Polymer	$[\eta]_\theta$ *dL/g anhydrous* 1,4-*dioxane* 30°*C*	$[\eta]$, *dL/g NaBr* 0.1 *M* 25°*C*	α	$\langle S_\theta^2 \rangle$ 1,4-*dioxane*, *cm* × 10^{12}	$\langle S^2 \rangle$ *NaBr* 0.1 *M cm* × 10^{-12}
PS-8	0.516	4.980	2.12	165	338
PS-11	0.178	0.930	1.73	54	104
PS-12	0.129	0.619	1.68	42	78
PS-17	0.098	0.407	1.60	32	58
PAA-1	0.203	1.212	1.81	65	128
PAA-2	0.179	1.005	1.77	58	111
P1	0.153	0.682	1.64	45	83
P2	0.120	0.547	1.65	38	70
P3		0.586		30	54
P4	0.151	0.455		19	31

of the K and a parameters of the Mark-Houwink equation for the copolymer sample P3 are as follows: $K = 6.15 \times 10^{-4}$ dL/g and $a = 0.65$ at 30°C in 1,4-dioxane (HPLC grade). The value of A is within the expected range: 654×10^{-11} cm. These results indicate that the P3 sample in solution has a semi-rigid conformation. The results in Table 2 indicate that the values of α increase from 1.6 to 2.1 with the increase of the molecular weight, as predicted by the theory.

As was expected, at θ-conditions the FFS, SF and Be models gave practically the same values for K_θ and B. At perturbed conditions all models gave different values for K and B. The FFS model results are the closest to those reported in literature [12, 17] for PAA. Using the obtained results we calculated the values of the other molecular parameters: A, b, R_0, σ and A_2. The values of A are valid only at θ-conditions, but, for comparison, we also calculated some values for A at perturbed conditions (see Tab. 3). The values

TABLE 3 Molecular parameters of polyacrylic acid

	Mark-Houwink constants		*Temperature*	*Rigidity coefficient*	*Steric coefficient*
Solvent	$K \times 10^4, dL/g$	a	$^\circ C$	σ	$A \times 10^{-4}\,cm$***
1,4-dioxane anh.*	8.50	0.500	30	1.83	730
Aq. sol. 1.5 M NaBr**	12.40	0.500	15	2.38	825
1,4-dioxane HPLC*	6.60	0.600	30		670
Aq. sol. 0.1 M NaBr*	3.12	0.755	25		520
Aq. sol. 1.5 M NaBr K	11.70	0.500	15	2.04	809
1,4-dioxane HPLC K	6.46	0.600	30		(665)
Aq. sol. 0.1 M NaBr K	5.24	0.755	25		(567)

* Ref. [12], ** Ref. [17], *** Calculated, *K*: This study.

of $\langle R_0^2 \rangle$ and of $\langle R^2 \rangle$ increase with the molecular weight and as was expected $\langle R^2 \rangle$ is larger than $\langle R_0^2 \rangle$ due to the expansion of the chain. The calculated from Krigbaum's equation values of the parameters A_2 and R_g for PAA in the present study were compared for similar molecular weights to the results obtained by light scattering in 1,4-dioxane (HPLC) at 26°C [9]. The calculated value of A_2 is 4.7×10^{-3} dL/g, while the experimental value obtained by light scattering is about 6.0×10^{-3} dL/g. In both cases A_2 is close to zero indicating that for the above mentioned conditions the solution is approaching the θ-conditions. The values of M_w for samples P3 and P4 obtained by GPC are 12,000 and 4,500 respectively. This indicates the presence of 150 repetitive AA/MA units and of 45 units of HEMA in average.

CONCLUSIONS

It was found that the commercial polymers P1 and P2 are PAA having a very low concentration of an acrylic precursor, P2 also contains traces of residual monomer. P3 is a co-polymer (AA/MA) of 2 : 1 ratio, while P4 is an oligomer of HEMA. The drying of the acrylic polymers by lyophilization results in the formation of cyclic anhydrides and/or chemical cross-linking, both in PAA and in P(AA/MA). The formation of intramolecular cyclic anhydrides does not reduce the solubility in water, whereas the formation of intermolecular anhydrides results in chemical cross-linking, which increases the molecular weight and the viscosity and thus decreases the solubility. The formation of the intramolecular cyclic anhydrides increases the rigidity of the chains and impedes the formation of aggregates in water solutions.

The FFS model gives the best fitting to the experimental results and can be successfully used to estimate the molecular parameters at perturbed conditions. The P1 and P2 polymers have flexible chains, whereas the P3 and P4 samples have semi-rigid chains at perturbed conditions.

REFERENCES

[1] Wilson, A. D. and Nicholson, J. W. (1993). *Acid-Base Cements: Their Biomedical and Industrial Applications*, Cambridge Univ., Cambridge.

[2] Kohn, D. H. and Ducheyene, P. (1992). In: "*Materials for Bone and Joint Replacement*", Chap. 2, p. 29, **14**, Causton, B. E. In: "*Medical and Dental Adhesives*", Chap. 8, p. 285, **14**, *Materials Science and Technology*, Cahn, R. W., Haasen, P. and Kramer, E. J. Eds., VCH, Cambridge.

[3] Lindén, L. A. (1996). *Polymeric Materials Encyclopedia*, Salamone, J. C. Ed., **3**, 1839, CRC Press, Boca Raton, Fl.

[4] Budd, P. (1989). In: "*Polyelectrolytes*", Comprehensive Polymer Science, **1**, C-11, Allen, G. and Bevigton, J. J. Eds., Pergamon Press Inc., New York.

[5] Dautzenberg, H. and Jeager, W. (1994). *Polyelectrolytes*, Hansen Pub., New York.

[6] Buscar

[7] Molyneux, P. (1983). *Water Soluble Synthetic Polymers: Properties and Behavior*, **1**, **2**, CRC Press, Boca Raton, Fl.

[8] Sperling, L. H. (1992). *Introduction to Physical Polymer Science*, John Wiley & Sons, New York.

[9] Newman, S., Krigbaum, W. R., Laugier, C. and Flory, P. J. (1954). *J. Polym. Sci.*, **15**, 451.

[10] Yamakawa, H., *Modern Theory of Polymer Solutions*, Harper's Chemistry Series, Harper and Row Pub., New York, 1971.

[11] Vera-Graziano, R., Martínez-Richa, A., Palacios-Alquisira, J., Barceló, F. and Castaño, V. M. (1999). *Macromol. Symp.*, **148**, 463.

[12] Flory, P. J. and Fox, T. G. Jr. (1951). *J. Am. Chem. Soc.*, **73**, 1904.

[13] Stockmayer, W. H. and Fixman, M. (1963). *J. Polym. Sci.*, **C1**, 137.

[14] Berry, G. C. (1967). *J. Chem. Phys.*, **46**, 1338.

[15] Krigbaum, W. R. (1955). *J. Polym. Sci.*, **18**, 315.

[16] Katime, I. (1994). *Química Física Macromolecular*, Universidad del País Vasco, Bilbao, Chap. 9.

[17] Brandrup, J. and Immergut, E. Eds. (1989). *Polymer Handbook*, John Wiley & Sons, New York.

[18] Benoit, H. C. (1997). In: "*A Half Century of the Journal of Polymer Science*", Tirrell, D. A. et al. Eds., John Wiley & Sons.

[19] Ward, Jr. (1981). *Chem. Ed.*, **58**, 867.

[20] Alvarez, C., Palacios, J. and Castaño, V. M., *Int. J. Polym. Mater.* (in press, 2000).

[21] Adamson, A. W. (1990). *Physical Chemistry of Surfaces*, 5th Edition, John Wiley & Sons, New York.

[22] Crisp, S., Kent, B. E., Lewis, B. G., Ferner, A. J. and Wilson, A. D. (1980). *J. Den. Res.*, **59**(6), 1055.

[23] Cutié, S. S., Smith, P. B., Henton, D. E., Staples, T. L. and Powell, C. (1997). *J. Polym. Sci., Part B, Polym. Phys.*, **35**, 2029.

[24] Wu, S., Jone, H. Ch. and Hwang, J. W. (1997). *J. Appl. Polym. Sci.*, **63**, 89.

[25] Nicholson, J. W. and Wilson, A. D. (1987). *British Polym. J.*, **19**, 67.

[26] Granger, D., In: "*Solid State NMR of Polymers*", pp. 179–200, Mathias, L. J. Ed., Plenum Press, New York, 1991.

[27] Coumou, C. (1996). *J. Colloid Sci.*, **15**, 408.