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PII: S0032-3861(97)00364-9

Polymer Vol. 39 No. 1, pp. 247–251, 1997
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0032-3861/97/$17.00+0.00

On the preparation of acrylic acid/vinyl acetate copolymers with constant composition—2. Refractive indexes for in-line evaluation of monomer conversion and copolymer composition

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(Revised 22 April 1997)

Refractive indexes are used to allow the in-line monitoring of acrylic acid (AA)/vinyl acetate (VA) copolymerizations in azeotropic solutions of ethanol and water (ETOH). It is shown that refractive indexes of AA and VA solutions in polar and non-polar solvents vary almost linearly with monomer volume fraction and that correlations for polymer refractive index increments obtained by measuring the refractive indexes of polymer solutions in different solvents do not allow precise evaluation of monomer conversion in homopolymerization reactions. A procedure which consists of obtaining the refractive index parameters in homopolymerization reactions and extending the results to copolymerizations is successfully implemented for AA/VA copolymerizations in ETOH, allowing the simultaneous in-line evaluation of both monomer conversion and copolymer composition. © 1997 Elsevier Science Ltd.

(Keywords: refractive index; acrylic acid; vinyl acetate)

Introduction

Copolymers of acrylic acid (AA) and vinyl acetate (VA) find successful applications in the mineral, textile, cosmetics, paper and oil industries and are also used as adhesives and for improving soil and water quality[1,2]. More recently, the use of acrylic acid/vinyl acetate copolymers is also being considered in certain processes which require precise control of copolymer composition, so that developing in-line techniques for adequate monitoring of reaction evolution is a very important task.

Although there is a lack of kinetic data regarding the AA/VA copolymerizations, it is well known that these systems are characterized by very different reactivity ratios (r_1 = 10.0, r_2 = 0.01)[3], (r_1 = 2.6, r_2 = 0.04)[4], which makes it difficult to control the copolymer composition in batch reactions. Heublein and coworkers[5–10] developed a technique for producing homogeneous AA/VA copolymers, with composition ranging from 5% to 90% of AA, which comprises the free-radical polymerization of AA/VA mixtures in buffered methanol/water solutions. According to the results obtained in our laboratories[11] though, copolymer properties were found to be too sensitive to process perturbations, so that alternative reaction schemes are under study[12]. Special attention has been given to semicontinuous and continuous free-radical polymerizations in ethanol/water solutions and in water/benzene suspensions. In all cases, the continuous monitoring of reaction evolution is fundamental for adequate control of copolymer composition to be attained.

The main objective of this paper is building an empirical model to correlate measured refractive index with monomer conversion and polymer composition data and showing that this correlations may be used for adequate and continuous monitoring of both monomer conversion and polymer composition in AA/VA reactions simultaneously. To our knowledge, this strategy has not been used before for in-line monitoring and control of copolymerization reactions. In order to do that, refractive indexes of solutions containing acrylic acid, vinyl acetate and AA/VA copolymers in different solvents, which have not been presented before, are presented and fitted to empirical models used with success in the literature previously.

Experimental procedure

Acrylic acid was bought from Carlo Erba, vinyl acetate was bought from Hoechst and benzoyl peroxide was bought from Merck. The other chemical species were commercial grades available in Habana. All liquid reagents were purified through distillation. Benzoyl peroxide was purified through recrystallization in methanol. Polymerizations were initiated by benzoyl peroxide and were carried out in 500 ml stirred tank reactors, under argon atmosphere, at 75°C. Refractive indexes at the wavelength λ = 546 nm were measured at 30°C in a Carl Zeiss–Jena refractometer, with precision of 0.0001. Samples were prepared by adding known volumes of each chemical species in graduated flasks of 100 ml. Monomer conversions were evaluated gravimetrically, by drying the polymer mass in vacuum ovens at ambient temperature, after precipitation in water (vinyl acetate rich polymers) or ethyl acetate (acrylic acid rich polymers) and centrifugation. Centrifugations were carried out for 10–15 min at 5000 rpm with a Janetzki centrifuge. Copolymer compositions were evaluated through potentiometric titration with NaOH in solutions of NaCl 0.05 M.

Results and discussion

As shown below, the in-line evaluation of monomer

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conversion and copolymer composition in copolymerization reactions by measuring the refractive index of the polymerization medium requires information regarding the variation of the refractive index of the binary monomer/solvent solutions and the ternary polymer/monomer/solvent solutions. For this reason, binary and ternary refractive index data are presented and analysed before applying the in-line monitoring technique to the copolymerization reactor.

Refractive indexes of binary monomer/solvent solutions. The procedure used here to develop the empirical model is similar to the one presented by Bahr and Pinto[13], which assumes that the refractive index of solvent/monomer mixtures may be given by:

$$\eta = \phi_s\eta_s + \phi_m\eta_m + A\phi_s\phi_m \qquad (1)$$

where ϕ_s and ϕ_m are the solvent and monomer volume fractions, η, η_s and η_m are the refractive indexes of the solvent/monomer solution, pure solvent and pure monomer and A is a constant which characterizes the binary solution. According to those authors, the empirical equation allowed easier and better fit of experimental data than theoretical models available in the literature. Volume fractions are preferred to describe the variation of refractive indexes of liquid solutions because, as shown by Lorimer[14], theoretical equations are linear in these variables.

Figures 1–4 show refractive indexes of solutions of AA and VA in water and benzene. It may be seen that refractive indexes vary almost linearly in these systems, so that equation (1) allows an excellent fit of experimental data. It is important to notice that benzene and water solutions present very different polar nature, which does not seem to be of much importance to explain refractive index variations in the case analysed. Similar results were obtained when other AA/VA solutions were prepared[15]. In these cases, the following values for the binary parameter A were obtained: $A_{VA/AA} = 0.00173$, $A_{ETOH/VA} = -0.00162$ and $A_{ETOH/VA} = 0.01176$, where ETOH represents solutions containing 93% in weight of ethanol and 7% in weight of water. (Ethanol/water solutions at 93/7 w/w are adequate solvents for AA/VA polymerizations because they dissolve both poly(acrylic acid), poly(vinyl acetate) and poly(acrylic acid-co-vinyl acetate) polymers. Besides, these solutions may be obtained by distillation as an azeotrope). Results confirm that refractive indexes may be assumed to vary almost linearly with solvent composition in the systems studied.

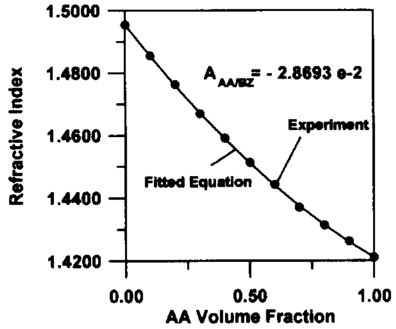

Figure 1 Refractive indexes of AA/benzene (BZ) solutions

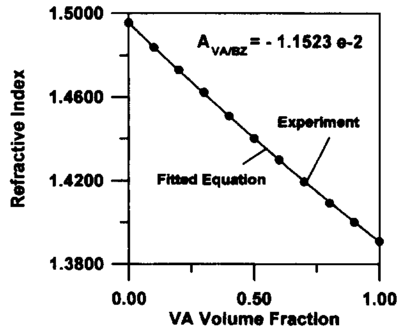

Figure 2 Refractive indexes of VA/benzene (BZ) solutions

Refractive indexes of ternary polymer/monomer/solvent solutions. In order to study the influence of polymer composition upon the refractive index of AA/VA polymer solutions, batch polymerization reactions were carried out in solutions of ethanol (93 wt.%) and water (7 wt.%) at 75°C. Conversion and refractive index results are shown in *Figure 5* and *Figure 6* as functions of time.

It is assumed here that refractive indexes of polymer solutions may be described by the following equations[13]:

$$\eta = \eta_s + \nu c_p + a c_p^2 \qquad (2)$$

$$\nu = \nu_1 + \nu_2\eta_s \qquad (3)$$

$$a = a_1 + a_2\eta_s \qquad (4)$$

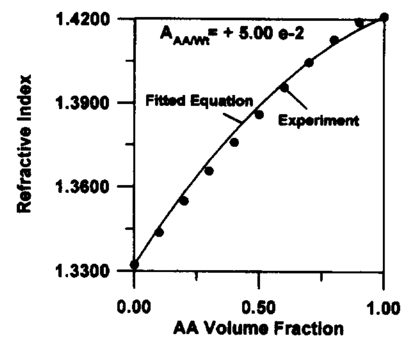

Figure 3 Refractive indexes of AA/water (Wt) solutions

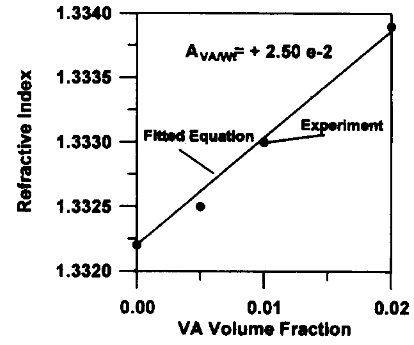

Figure 4 Refractive indexes of VA/water (Wt) solutions

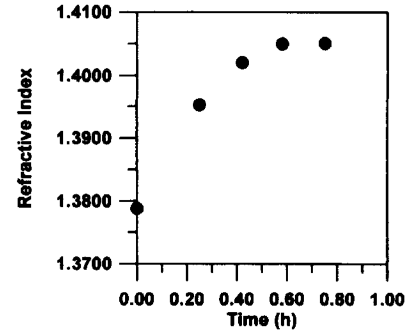

Figure 5 Refractive indexes for the batch AA homopolymerization. ($\phi^o_{AA} = 0.30$, $c_{io} = 9.50 \times 10^{-3}$ mol l^{-1})

where a_1, a_2, ν_1 and ν_2 are parameters which characterize the polymer species and c_p is the polymer concentration in grams per mililitre. Assuming that volume additivity holds and that final polymer concentration is not large, it is possible to write the following equations for the batch AA homopolymerization:

$$c_{\mathrm{p}}=\frac{M_{\mathrm{PAA}}}{V_{\mathrm{ETOH}}+V_{\mathrm{AA}}+V_{\mathrm{PAA}}}=\phi^{o}_{\mathrm{AA}}\rho_{\mathrm{AA}}x \qquad (5)$$

$$\eta_{\mathrm{s}}=\frac{\phi^{o}_{\mathrm{ETOH}}}{\phi^{o}_{\mathrm{ETOH}}+\phi^{o}_{\mathrm{AA}}(1-x)}\eta_{\mathrm{ETOH}}+\frac{\phi^{o}_{\mathrm{AA}}(1-x)}{\phi^{o}_{\mathrm{ETOH}}+\phi^{o}_{\mathrm{AA}}(1-x)}\eta_{\mathrm{AA}}+\frac{A_{\mathrm{ETOH/AA}}\phi^{o}_{\mathrm{ETOH}}\phi^{o}_{\mathrm{AA}}(1-x)}{(\phi^{o}_{\mathrm{ETOH}}+\phi^{o}_{\mathrm{AA}}(1-x))^2} \qquad (6)$$

where M is mass, V is volume, x is the monomer conversion, ρ is the density, ϕ° is the initial volume fraction and PAA refers to poly(acrylic acid). Neglecting the quadratic contribution, as polymer concentrations are assumed to be small, and substituting equations (3), (5) and (6) into equation (2), it is possible to evaluate monomer conversion by monitoring the refractive index of the polymer solution, if the parameters a_1, a_2, ν_1 and ν_2 are known. It is assumed that initial volume fractions, refractive indexes and densities of the pure monomer and solvent, and the binary coefficient are known.

Based on data presented by Brandrup and Immergut[17] and Iglesias and Pinto[15] concerning the refractive index of PAA solutions in water, dioxane and ethanol/water solutions, it is possible to write equation (3) as (see *Figure 7*):

$$\nu_{\mathrm{PAA}}=1.13885-0.74061\eta_{\mathrm{s}} \qquad (7)$$

Assuming that equation (7) is valid and that a_1 and a_2 are equal to zero (quadratic terms), the refractive indexes presented in *Figure 5* can be used with equation (2) to allow the evaluation of monomer conversions. Results are shown in *Figure 8*. It may be seen that experimental conversions are smaller than conversions estimated with equation (2) in this case. However, as conversion varies almost linearly with the refractive index, results can be improved by simply fitting a straight line to the experimental values. This is equivalent to assuming that the parameters ν_1 and ν_2 are unknown and re-evaluating the parameters of equation (3), based on the specific experimental data available in *Figure 5* and 6. In this case, equation (3) becomes;

$$\nu_{\mathrm{PAA}}=2.0630-1.4073\eta_s \qquad (8)$$

which allows the perfect fit of the experimental data presented in *Figures 5 and 6*, as shown in *Figure 8*, but does not lead to adequate description of the data presented in *Figure 7*. Therefore, if monomer conversion is to be estimated for the system AA/ETOH, data obtained for PAA refractive index increments in other solvents is of no use. However, if homopolymerization data is used to calibrate the empirical model, excellent agreement between experimental and model results may be attained.

A similar procedure may be used to analyse the VA homopolymerization. *Figures 9* and *10* show refractive indexes and conversions as a function of time for VA homopolymerization in ETOH.

Bahr and Pinto[13] studied the refractive index of PVA solutions in different solvents and showed that

$$\nu_{\mathrm{PVA}}=1.1837-0.8000\eta_{\mathrm{s}} \qquad (9)$$

Similarly, when the refractive index data of *Figure 9* and equation (9) are used with equation (2) to allow the prediction of the VA conversion data presented in *Figure 10*, *Figure 11* shows that experimental results are larger than model predictions. Again, available experimental data may be used to re-evaluate the refractive index parameters, which allows perfect agreement between experimental and

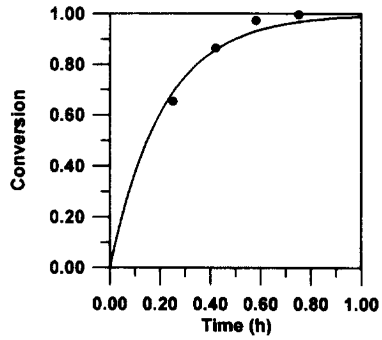

Figure 6 Monomer conversion for the batch AA homopolymerization. ($\phi^o_{\mathrm{AA}}=0.30$, $c_{io}=9.50\times10^{-3}\ \mathrm{mol\ l^{-1}}$)

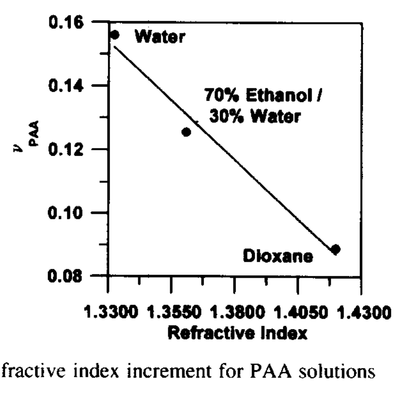

Figure 7 Refractive index increment for PAA solutions

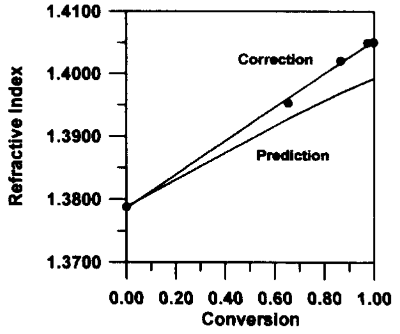

Figure 8 Refractive index as a function of conversion for the batch AA homopolymerization

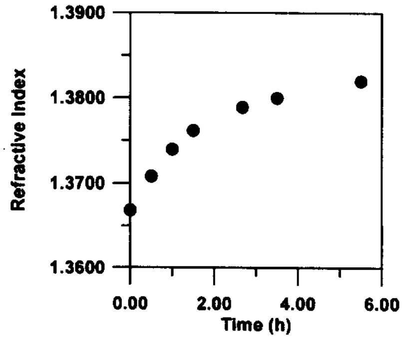

Figure 9 Refractive indexes for the batch VA homopolymerization. ($\phi^o_{VA}=0.30$, $c_{io}=1.24\times10^{-2}\ \mathrm{mol\ l^{-1}}$)

model results. Then, equation (3) can be written as:

$$\nu_{\mathrm{PVA}} = 2.3128 - 1.6366\eta_{\mathrm{s}} \qquad (10)$$

Sensitivity analysis. Results obtained show that refractive index increments obtained in other solvents cannot be used to allow the evaluation of monomer conversions in a particular reaction system. This is likely to be true in other polymerization systems because monomer conversions are very sensitive to small changes of ν. Small errors introduced when equation (3) is used to describe refractive indexes of polymer solutions obtained in different solvents may lead to gross errors when conversions are estimated in a particular polymerization system. If the monomer feed fraction is small, according to equations (2)–(6) it may be written:

$$\frac{\mathrm{d}\eta}{\mathrm{d}x} \approx \nu^{o} cp_{\mathrm{f}} - \alpha\eta_{\mathrm{M}}(1 + 2\nu_1 cp_{\mathrm{f}}) \qquad (11)$$

where

$$\alpha = \phi^{o}_{\mathrm{M}} \frac{(\eta_{\mathrm{M}} - \eta_{\mathrm{s}})}{\eta_{\mathrm{M}}} \qquad (12)$$

ν° is the initial refreactive index increment and cp_{f} is the final polymer concentration. Therefore, the larger the difference between the refractive indexes of solvent and monomer species and the larger the monomer feed fractions, the more sensitive conversion predictions are to small variations of the coefficients of equation (3). This may explain why conversion prediction errors were larger for the PAA than for the PVA homopolymerization (see *Figures 8, and 11*). If the coefficients are subject to variations of 10%, at the conditions analysed conversion prediction errors are about 30%. However, when equation (7) and (9) are compared to equation (8) and (10) it may be seen that differences of individual coefficients may be even greater than 10%.

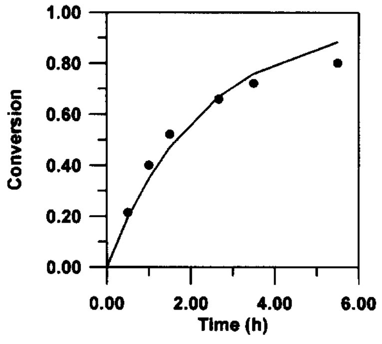

Figure 10 Monomer conversion for the batch VA homopolymerization. ($\phi^{o}_{\mathrm{VA}} = 0.30$, $c_{io} = 1.24 \times 10^{-2}$ mol l^{-1})

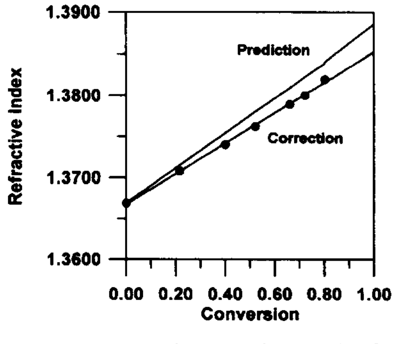

Figure 11 Refractive index as a function of conversion for the batch VA homopolymerization.

In-line monitoring of copolymerization reactions. In order to analyse whether homopolymerization data may be extended to copolymerizations, refractive index equations are extended[13], based on the same assumptions made previously for the homopolymerizations. Then:

$$c_{\mathrm{pAA}} = \phi^{o}_{\mathrm{AA}}\rho_{\mathrm{AA}}x_{\mathrm{AA}} \qquad (13)$$

$$c_{\mathrm{pAA}} = \phi^{o}_{\mathrm{VA}}\rho_{\mathrm{VA}}x_{\mathrm{VA}} \qquad (14)$$

$$\begin{aligned}
\eta_2 = {} & \frac{\phi^{o}_{\mathrm{ETOH}}}{\phi^{o}_{\mathrm{ETOH}} + \phi^{o}_{\mathrm{AA}}(1 - x_{\mathrm{AA}}) + \phi^{o}_{\mathrm{VA}}(1 - x_{\mathrm{VA}})}\eta_{\mathrm{ETOH}} + \\
& \frac{\phi^{o}_{\mathrm{AA}}(1 - x_{\mathrm{AA}})}{\phi^{o}_{\mathrm{ETOH}} + \phi^{o}_{\mathrm{AA}}(1 - x_{\mathrm{AA}}) + \phi^{o}_{\mathrm{VA}}(1 - x_{\mathrm{VA}})}\eta_{\mathrm{AA}} + \\
& \frac{\phi^{o}_{\mathrm{VA}}(1 - x_{\mathrm{VA}})}{\phi^{o}_{\mathrm{ETOH}} + \phi^{o}_{\mathrm{AA}}(1 - x_{\mathrm{AA}}) + \phi^{o}_{\mathrm{VA}}(1 - x_{\mathrm{VA}})}\eta_{\mathrm{VA}} + \\
& \frac{A_{\mathrm{ETOH/AA}}\phi^{o}_{\mathrm{ETOH}}\phi^{o}_{\mathrm{AA}}(1 - x_{\mathrm{AA}})}{(\phi^{o}_{\mathrm{ETOH}} + \phi^{o}_{\mathrm{AA}}(1 - x_{\mathrm{AA}}) + \phi^{o}_{\mathrm{VA}}(1 - x_{\mathrm{VA}}))^2} + \\
& \frac{A_{\mathrm{ETOH/VA}}\phi^{o}_{\mathrm{ETOH}}\phi^{o}_{\mathrm{VA}}(1 - x_{\mathrm{VA}})}{(\phi^{o}_{\mathrm{ETOH}} + \phi^{o}_{\mathrm{AA}}(1 - x_{\mathrm{AA}}) + \phi^{o}_{\mathrm{VA}}(1 - x_{\mathrm{VA}}))^2} + \\
& \frac{A_{\mathrm{VA/AA}}\phi^{o}_{\mathrm{VA}}\phi^{o}_{\mathrm{AA}}(1 - x_{\mathrm{AA}})(1 - x_{\mathrm{VA}})}{(\phi^{o}_{\mathrm{ETOH}} + \phi^{o}_{\mathrm{AA}}(1 - x_{\mathrm{AA}}) + \phi^{o}_{\mathrm{VA}}(1 - x_{\mathrm{VA}}))^2} \qquad (15)
\end{aligned}$$

$$\eta = \eta_{\mathrm{s}} + \nu_{\mathrm{PAA}}c_{\mathrm{pAA}} + \nu_{\mathrm{PVA}}c_{\mathrm{pVA}} \qquad (16)$$

where x_{AA} and x_{VA} are the individual AA and VA conversions to be evaluated from refractive index measurements and the other parameters are known. If initial monomer compositions are known, individual monomer conversions allow the computation of global monomer conversion and copolymer composition as

$$x = f^{o}_{\mathrm{AA}}x_{\mathrm{AA}} + f^{o}_{\mathrm{AA}}x_{\mathrm{VA}} \qquad (17)$$

$$F_{\mathrm{AA}} = \frac{f^{o}_{\mathrm{AA}}x_{\mathrm{AA}}}{f^{o}_{\mathrm{AA}}x_{\mathrm{AA}} + f^{o}_{\mathrm{VA}}x_{\mathrm{VA}}} \qquad (18)$$

where F_{AA}, f^{o}_{AA} and f^{o}_{VA} are respectively the mass (molar) content of AA in the final polymer, and the mass (molar) fraction of AA and VA in the initial monomer feed.

As at each sampling time just a single value is measured (η) and two additional values are to be computed (x_{AA} and x_{VA}), an additional constraint is needed. The additional constraint used here is the classical Mayo–Lewis equation, used to describe the compolymerization kinetics

$$\frac{\mathrm{d}x_{\mathrm{AA}}}{\mathrm{d}x_{\mathrm{VA}}} = \frac{r_1 f^{o}_{\mathrm{AA}}(1 - x_{\mathrm{AA}})^2 + f^{o}_{\mathrm{VA}}(1 - x_{\mathrm{AA}})(1 - x_{\mathrm{VA}})}{r_2 f^{o}_{\mathrm{VA}}(1 - x_{\mathrm{VA}})^2 + f^{o}_{\mathrm{AA}}(1 - x_{\mathrm{AA}})(1 - x_{\mathrm{VA}})} \qquad (19)$$

so that additional experimental information is not fundamental for monitoring the copolymerization. Reactivity ratios may be found in the literature[4].

Figure 12 shows a large collection of experimental data obtained for batch and continuous AA/VA copolymerizations in ETOH, carried out with different feed compositions, so that individual monomer conversions and polymer

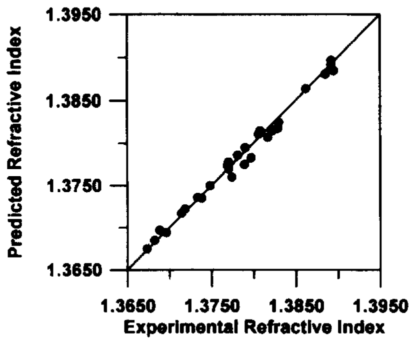

Figure 12 Predicted and experimental refractive index in AA/VA copolymerizations [16]

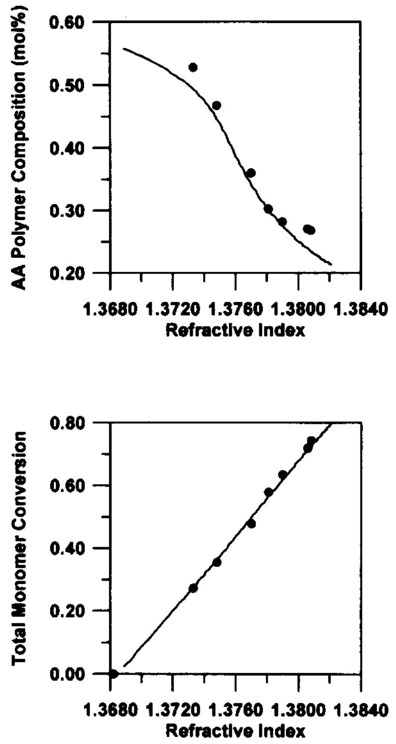

Figure 13 Copolymer composition and monomer conversion as functions of measured refractive index ($\phi^{0}_{\mathrm{AA}} = 0.04$, $\phi^{0}_{\mathrm{VA}} = 0.26$, $c_{\mathrm{io}}1.24 \times 10^{2} \mathrm{mol\,l^{-1}}$)

compositions varied uniformly in the interval (0,1)[16]. As it may be observed, agreement is very good. Conversion and composition errors were always smaller than 5%, as shown in *Figure 13* for a batch reaction. Therefore, it may be said that both monomer conversion and polymer composition may be computed in-line through refractive index measurements in AA/VA copolymerizations in ETOH, which may lead to the development and actual implementation of advanced techniques to control the quality of the final polymer resin. The procedure carried out here may be easily implemented in other copolymerization systems.

Conclusions

Refractive indexes of AA and VA solutions with polar and non-polar solvents vary almost linearly with monomer volume fraction. The largest nonlinear interaction coefficient obtained for seven binary systems analysed was equal to 5.00×10^{-2} for solutions of AA in water. For polymer compositions below 0.3 g ml^{-1}, it was also shown that refractive indexes of PAA and PVA solutions in ETOH vary mostly linearly with polymer composition. Based on published and measured data, PAA refractive index increments were then obtained as a function of the refractive index of the solvent.

Although available correlations allow the computation of the refractive index increments of polymer solutions as a function of solvent refractive index, the high sensitivity of conversion prediction to small variations of the equation coefficients may lead to large conversion prediction errors when such equations are used to evaluate monomer conversion in-line during homopolymerizations. However, it was shown that homopolymerization data may be used to allow the estimation of the parameters for the specific system under study and that the parameters obtained may be used to allow the in-line evaluation of both monomer conversion and copolymer composition in copolymerizations. The procedure was implemented successfully for AA/VA copolymerization reactions in ETOH.

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