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Prediction of copolymer composition drift using artificial neural networks: copolymerization of acrylamide with quaternary ammonium cationic monomers

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The free radical copolymerization of acrylamide with a quaternary ammonium cationic comonomer, diethylaminoethyl acrylate (DMAEA), has been investigated in inverse-emulsion. The copolymer composition was determined from residual monomer concentrations using an h.p.l.c. method. Both reactivity ratios were observed to change with conversion. Furthermore, the reactivity ratio of the cationic monomer was found to be a function of the ionic strength and monomer concentration and, to a limited extent, the polymer concentration and the organic-to-aqueous phase ratio. Therefore, the classical binary ultimate group copolymerization scheme cannot predict copolymer composition drift throughout the reaction. An artificial neural network (ANN) has been built to predict the copolymer composition. ANNs have the ability to map nonlinear relationships without *a priori* process information. The results show that an ANN can predict the copolymer composition very well as a function of reaction conditions and conversion. It is expected that for any system where the reactivity ratios are conversion dependent that an ANN, such as the one developed herein, will be preferable. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: acrylamide; artificial neural network; copolymer composition; copolymerization; dimethylaminoethyl acrylate; reactivity ratios)

INTRODUCTION

Copolymers of acrylamide with quaternary ammonium monomers are applied in several aqueous solid–liquid separations such as fines retention in paper making, and as flocculants and biocides in municipal and industrial water treatment[1,2]. Cationic copolymers are characterized by their copolymer composition or charge density, molecular weight and chain architecture. Of these molecular parameters, the copolymer composition is perhaps the most important variable influencing the efficiency of flocculation. Because there are no analytical methods which can estimate the copolymer composition in a rapid fashion, either directly or indirectly through monomer composition, a mathematical model is needed to estimate the copolymer composition if one wishes to control the copolymer composition on-line during a polymerization. The classical binary copolymerization model is often used to predict the polymer composition according to the functionality of the ultimate group on the chain. According to the classical kinetic approach, the chemical composition is determined by only two kinetic parameters, the monomer reactivity ratios[3–8]. However, various researchers have obtained different reactivity ratios for the same monomer pair. This is partly due to the correlation between r_1 and r_2 and the difficulty in obtaining statistically independent estimates. *Table 1* lists the reactivity ratios of acrylamide with diallyldimethylammonium chloride (DADMAC) from the literature. These data show that reactivity ratios change with reaction conditions in a nonrandom fashion. For example, Wandrey[11] observed that reactivity ratios are dependent on the feed ratio, while Baade[9] found that the reactivity ratio of both monomers increased slightly with increasing monomer concentration. Reichert determined that the reactivity of the cationic monomers increased with the ionic strength of the aqueous phase[12] owing to shielding of the electrostatic repulsive forces. Their results are contrary to the assumptions of the classical copolymer model.

Johnson *et al.*[13] expressed doubts as to constancy of the monomer reactivity ratios at high conversions in the free radical copolymerization of styrene and methyl methacrylate, where a change in the monomer reactivity ratios was observed, particularly with the onset of the gel effect. Johnson's results were reproduced by Dionisio and O'Driscoll[14]. In the copolymerization of acrylamide with dimethylaminoethyl methacrylate sulfate, Gromov[15] found that the monomer and polymer compositions were virtually independent of the extent of the reaction up to 50–70% conversion of both monomers. However, the reactivity ratios changed significantly. For example, at low conversion ($X < 15\%$), r_1(acrylamide) $= 0.52 \pm 0.05$ and $r_2 = 1.9 \pm$

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Table 1 Comparison of the reactivity ratios determined by various authors for the copolymerization of acrylamide with DADMAC

r_1	r_2	Monomer concentration (mol l^{-1})	Temperature (°C)	f_1	Ref.
6.4 ± 0.4	0.06 ± 0.03	0.5	50	0.3–0.7	[9]
6.7	0.58	1.5	20	0.1–0.9	[10]
6.62[a]	0.074[a]	3.0	35	0.11–0.89	[11]
714[a]	0.22[a]	4.0	35	0.2–0.72	[11]
7.54[b]	0.049[b]	5.75	47	0.2–0.8	[12]

[a] These are average values, since r_1 and r_2 were observed to depend on the feed ratio
[b] Determined in inverse-emulsion polymerization

0.2 while at high conversion (70 ~ 75%), $r_1 = 0.18$ and $r_2 = 5.6$.

Experimental deviations from the predictions of the ultimate copolymerization kinetic model have prompted the development of alternative schemes, all of which use more parameters than the binary reactivity ratios. Such models are often very complex[16], with as many as eight parameters which need to be simultaneously estimated. In general, alternative models are impractical, at least from a statistical parameter estimation point of view. In the present work, the copolymerization of acrylamide (AAM) with dimethylaminoethyl acrylamide quaternized with methyl chloride (DMAEA) has been studied. The copolymer composition was estimated from the residual monomer concentrations using an h.p.l.c. method[17]. An artificial neural network (backpropagation network) has been built to predict the copolymer composition.

EXPERIMENTAL

The polymerizations were carried out using an inverse-emulsion procedure in a 5-L 316-stainless steel, stirred, tank reactor. The polymerizations were performed isothermally at 30, 35, 40, and 45°C, while the monomer concentrations were kept at 50 wt% of the aqueous phase. The acrylamide–comonomer feed ratio was varied between 0.5 and 0.95. The initiator was azocyanovaleric acid (ACV, Wako Chemical Co.) and was used as received without further purification. The reactant mixture was agitated at 400 r.p.m. throughout the course of the polymerization.

The acrylamide monomer (AAM) was purchased from Cytec (Charlotte, NC), and was used either as received or after recrystallization from chloroform (Fisher ACS Reagent Grade, 99.9% pure, Norcross, GA). The DMAEA quaternary ammonium monomer was obtained from CPS Chemicals (West Memphis, AR) as an aqueous solution (80%) inhibited with approximately 600 ppm of hydroquinone monomethylether and was purified by repeated extractions and crystallization from acetone. For the polymerization in inverse-emulsion, the aqueous phase was emulsified in Isopar-M (Exxon, supplied by ChemCentral, Nashville, TN), a narrow cut of an isoparaffinic mixture. The nonionic stabilizers Hypermer B239 (a block copolymeric surfactant), Arlacel 83 (sorbitan sesquioleate) and TWEEN 85 (polyoxyethylene sorbitan trioleate), were gifts from ICI Americas (Wilmington, DE), and were used without purification. The phase ratio (w:o vol/vol) was varied from 0.8/1 to 1.8/1 with the oil phase containing 6–8 wt% stabilizer.

Type I reagent grade water with a resistance ≥ 18 MΩ-cm was obtained through a series of deionization and organic scavenger cartridges (Continental Water Systems Corp.). Nitrogen, with a purity of 99.99%, was purchased from Liquid Air, Inc. (Nashville, TN) and was used to strip out the residual dissolved oxygen. The oxygen purging procedure included 15 min independent sparging of the aqueous and organic phase, and a final 30 min following the water-in-oil emulsification in the reactor. Residual dissolved oxygen levels were reduced to below 1 ppm, as determined by an Ingold DO probe.

Twenty-millilitre aliquots were withdrawn from the reactor periodically at 2-min intervals at low conversions and in 5–10-min intervals at high conversions in presterilized 20 mL glass scintillation vials (Fisher Scientific) containing 100 ppm of hydroquinone. The hydroquinone was used to terminate the reaction by scavenging residual free radicals. These samples were then stored in ice water for the remainder of the reaction and then transferred to a refrigerator where they were maintained below 10°C until they were analysed, usually the following day.

An h.p.l.c. method was developed for the determination of the copolymer composition by measuring the residual concentration of both monomers[17]. A small amount of sample (0.01–0.02 g) of this aliquot was added to 10 mL mobile phase (mixture of acetonitrile and deionized water) and agitated. Then the polymer and oil in the mobile phase containing the aliquot sample was separated by high-speed centrifugation for 2 min. Following the centrifugation the samples were diluted using the mobile phase to provide a residual monomer

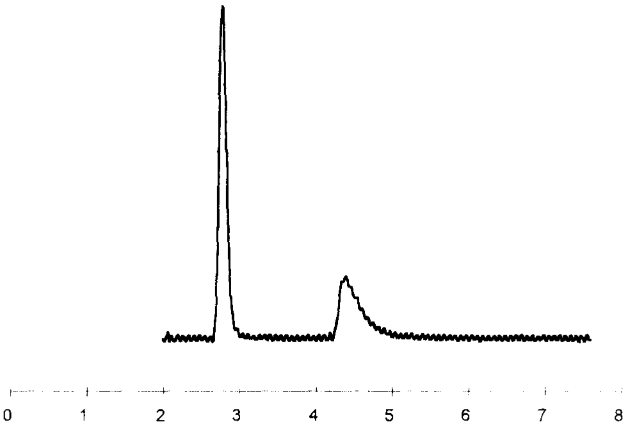

Figure 1 An example of an h.p.l.c. chromatogram for a system AAM/DMAEA consisting of 100 ppm of acrylamide and 100 ppm of DMAEA over a C_{18} coated silica gel sorbent. The mobile phase was 90 vol% acetonitrile, 10 vol% water with 0.05 mol dibutylamine. The pH of mobile phase was adjusted to 7.0

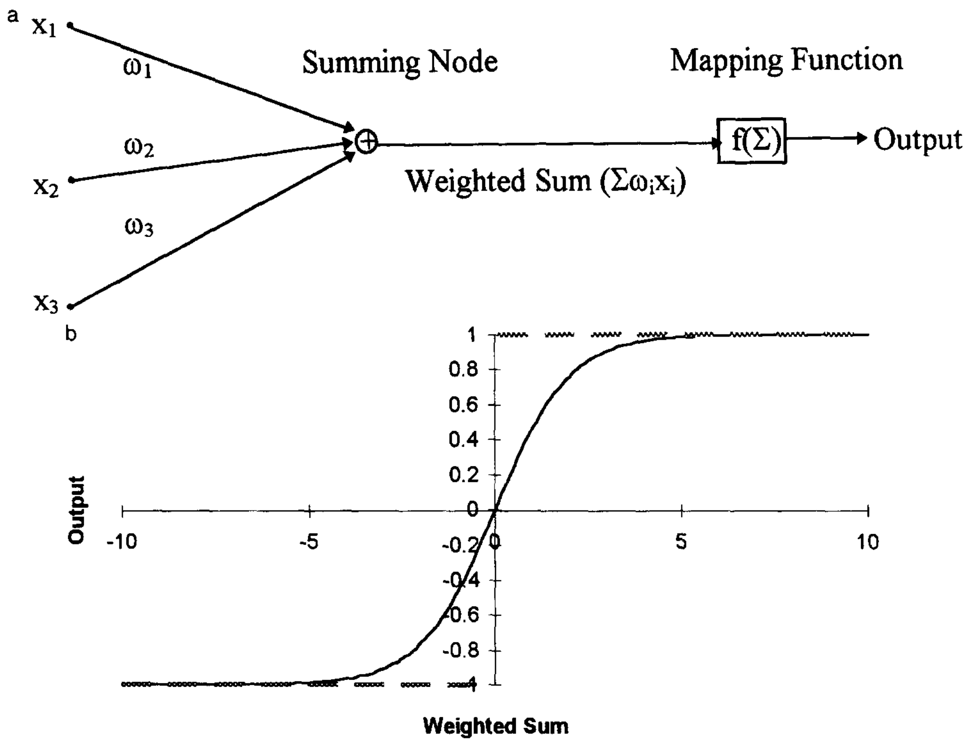

Figure 2 (a) Diagram of single-node backpropagation network. (b) Sigmoid mapping function within an artificial neurone

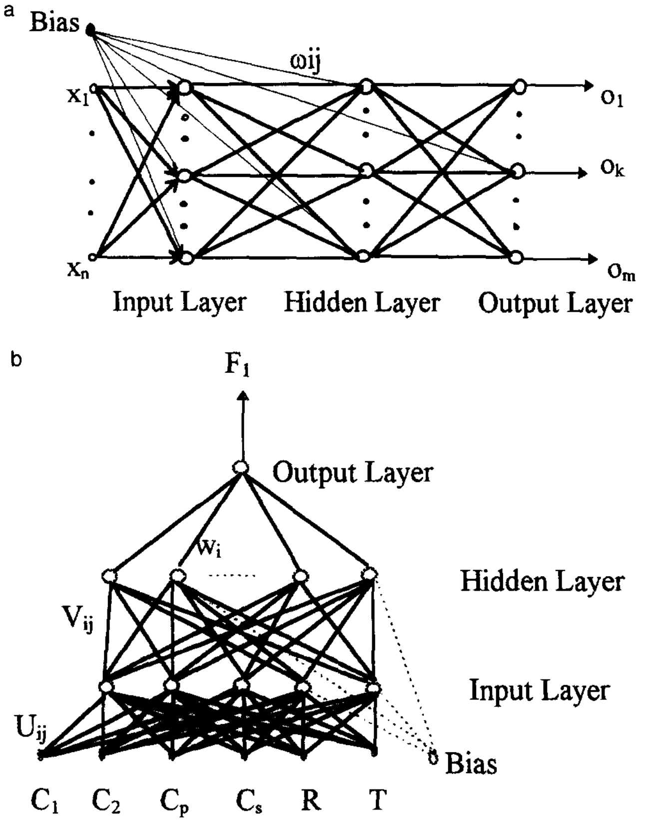

Figure 3 (a) The general structure of a three layer backpropagation (BP) network. $x_1 \ldots x_n$ are input variables. $o_1 \ldots o_m$ are outputs. (b) The structure of the backpropagation network used for copolymer composition prediction. C_1 is the AMM concentration (wt%), C_2 is the DMAEA concentration (wt%), C_p is the copolymer concentration (wt%), C_s is the surfactant concentration (wt%), R is the aqueous phase weight fraction and T is the reaction temperature (°C). The output, F_1 is the instantaneous copolymer composition

concentration between 10 and 200 ppm and injected into the h.p.l.c.. The injection volume was 200 μL with every sample being measured three to five times. *Figure 1* shows an example of an h.p.l.c. chromatogram for the AAM/DMAEA system. The h.p.l.c. was calibrated with standard solutions of the monomers. For AAM, the calibration curve was linear between 1 and 200 ppm, while for DMAEA, the calibration curve is linear between 1 and 500 ppm. The method is further detailed in a paper by Hunkeler *et al.*[17]. The monomer concentrations as determined by h.p.l.c., were used to train the artificial neural network.

ARTIFICIAL NEURAL NETWORK FOR COPOLYMER COMPOSITION PREDICTION

Artificial neural networks have evolved from research aimed at modelling cell activity in brain tissue. The basic processing elements of neural networks are called artificial neurones, or simply nodes. The neuron is actually a complex computing device which performs summation and nonlinear mapping functions. *Figure 2a* shows the diagram of a neuron. Any function, f(x), can be used as the nonlinear mapping function. A sigmoid function is usually used for the node mapping function, as is shown in *Figure 2b*. Neurones normally operate in parallel and are configured in a regular architecture. They are often organized in layers, and feedback connections both within the layer and toward adjacent layers are allowed. *Figure 3a* shows the general structure of a three-layer backpropagation (BP) network, which is a feedforward network (no feedback connection), consisting of input layer, hidden layer and output layer.

The number of nodes in the input layer is usually equal to the number of input variables. Similarly, the node number in the output layer equals the number of output variables. The number of nodes in the hidden layer is one of the most important considerations when solving problems using multilayer feedforward networks. In general, the more exemplars, the greater the number of hidden units, and the more precise the system. However, if the number of nodes in the hidden layer is too large, the system will be over-trained and will fit the error in the data. The 'bias' in *Figure 3a* actually is a fixed input, −1, which functions as the constant term in polynomial. The strength of each connection is expressed by a numerical value, ω_{ij}, called a weight, which can be adjusted. If the connection weights on a input variable are large, the connection to this variable is strong, and this variable will have significant effect on the outputs.

There are many applications of neural networks[18–20]. Neural 'nets' are mathematical models that have the ability to 'learn' the correlation between input and output values. Training the neural net to learn consists of presenting it with a set of correlated inputs and outputs, called exemplars. The objective for the network is to model the relationship between input and output variables. The system learns by adjusting the weights (ω_{ij}) of the node connection. The most extensively adopted learning algorithm is the backpropagation algorithm[21], which is a generalization of the steepest descent method. It consists of minimizing the mean square error (E), defined as:

$$E = \sum_{l=1}^{r}\sum_{k=1}^{m}[d_k^l - o_k^l]^2 \tag{1}$$

by adjusting each connection ω_{ij} where d_k comes from the r input–output pairs of exemplar data (x_k, d_k) available for training the network and o_k is the network output corresponding the input variable x_k. The individual weight adjustment is as follows:

$$\Delta\omega_{ij} = -\eta\frac{\partial E}{\partial\omega_{ij}} \tag{2}$$

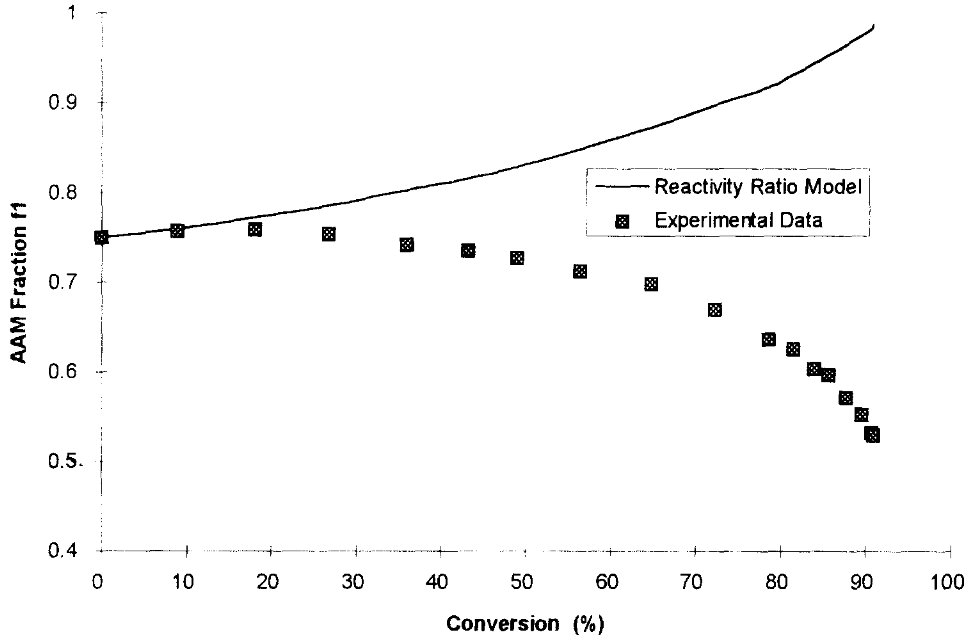

Figure 4 A comparison of the predictions of the reactivity ratio model and experimental data for an acrylamide/DMAEA copolymerization under the following conditions: $[AAM]_0 = 375\,g\,L_w^{-1}$, $[DMAEA]_0 = 125\,g\,L_w^{-1}$, $T = 45^\circ C$, phase ratio = 1/1 (vol/vol), [surfactant] = 5 wt%, and the agitation rate was 400 r.p.m.

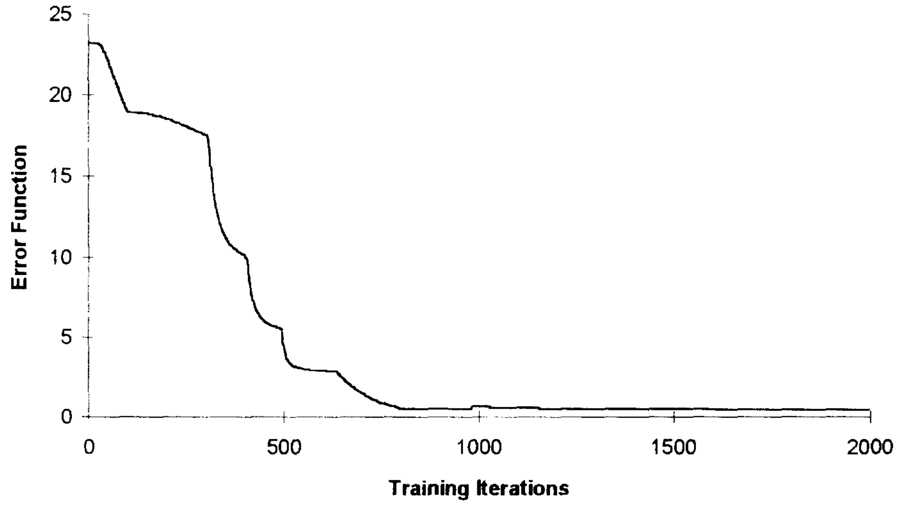

Figure 5 The profile of the error function ($1/2\Sigma e_i^2$) during the training process of the ANN

Table 2 The experimental conditions of the 11 copolymerization reactions that were used to generate data for training of the artificial neural network

T (°C)	Phase ratio (aq. wt fraction)	f_{10}	Total mixture weight (g)	Surfactant (wt%)	Initiator (g)	Monomer wt% in aqueous phase
30	0.50	0.5	2000	4	0.1	50
30	0.55	0.5	2000	4	0.1	50
30	0.60	0.5	2000	4	0.1	50
35	0.50	0.7	2000	4	0.1	50
35	0.55	0.7	2000	5	0.1	50
35	0.60	0.7	2000	5	0.1	50
40	0.50	0.9	2000	5	0.1	50
40	0.55	0.9	2000	5	0.1	50
40	0.60	0.9	2000	5	0.1	50
45	0.50	0.6	2000	5	0.1	50
45	0.55	0.8	2000	5	0.1	50

Table 3 Partial list of the 275 training exemplars

C_1	C_2	C_p	C_s	T	R	F_1
25	25	0	4.0	35	0.6	0.467
19.35	19	11.66	4.0	35	0.55	0.478
14.75	13.48	21.77	4.0	30	0.5	0.492
4.1	3.4	42.5	4.5	35	0.6	0.603
2.91	2.55	44.5	4.5	30	0.55	0.568
38.48	7.12	4.4	5.0	45	0.55	0.702
32.6	5.23	12.17	5.0	45	0.55	0.762
20.8	2.53	26.67	5.0	45	0.55	0.842
9.8	1.05	39.15	5.0	45	0.55	0.89
6.6	0.6	42.74	5.0	45	0.55	0.882
30.45	9.48	10.12	4.5	35	0.5	0.61
22.6	6.12	21.3	4.5	35	0.5	0.721
19.8	4.9	26.2	4.5	35	0.5	0.717
16.5	3.85	29.65	4.5	35	0.5	0.756
13.7	3.15	33.15	4.5	35	0.5	0.804
7.42	1.62	40.96	4.5	35	0.5	0.837
25.6	7.34	17.06	4.0	35	0.6	0.724
13.41	3.0	23.59	4.0	35	0.6	0.813
27.3	12.2	10.52	4.0	45	0.55	0.676
25.13	11.02	13.85	4.0	45	0.55	0.665
22.9	10	17.1	4.0	45	0.55	0.64
15.6	6.11	28.3	4.0	45	0.55	0.68
12.08	4.66	33.26	4.0	45	0.55	0.693
6.48	2.37	41.15	4.0	45	0.55	0.76
22.8	15.4	11.8	5.0	35	0.6	0.574
18.9	11.6	19.5	5.0	35	0.6	0.568
15.24	8.4	26.36	5.0	35	0.6	0.598
12.54	6.46	31.0	5.0	35	0.6	0.62
10.47	5.04	34.49	5.0	35	0.6	0.654

Table 4 Connection weights in the input layer of the copolymer composition prediction network

	Node 1	Node 2	Node 3	Node 4	Node 5	Node 6
C_1	−3.661	−1.359	1.462	−0.6477	−0.1498	−0.2976
C_2	0.7139	−1.6379	−1.2128	−1.337	0.3891	−2.106
C_p	0.049	0.046	−0.228	0.153	−0.082	0.233
C_s	−0.049	0.0416	0.0028	0.015	−0.0815	0.0423
R	0.0036	−0.026	0.019	0.0074	0.0314	−0.0533
T	−0.229	0.11	0.071	0.072	0.019	0.101

where η is the learning constant with a value of between 0.1 and 1.0, which influences the effectiveness and convergence during training process. In general, the optimum value of η depends on the problem being solved, and only small learning constants guarantee a true gradient descent.

In this study, a three-layer backpropagation network (BP) was built, in which there are six nodes in the input layer, 10 nodes in the hidden layer, and only one node in the output layer. *Figure 3* shows the structure of this BP network, in which w_i is the connection weight between the output layer and the ith node in the hidden layer, v_{ij} is the connection weight between ith node in the hidden layer and jth node in the input layer, and u_{ij} is the connection weight between the ith node in the input layer and the jth input variable. The AAM concentration (C_1), DMAEA concentration (C_2), copolymer concentration (C_p), phase ratio (R) (aqueous phase weight fraction), temperature (T), and the surfactant concentration (C_s), comprise the input signals. The output is the instantaneous copolymer composition (F_1), from which the cumulative copolymer composition ($\bar{F}_1$) can be easily computed.

RESULTS AND DISCUSSION

In general, reactivity ratios are estimated from the experimental data generated from dilute solution copolymerizations[9-11] at low conversions. Baade *et al.*[9] obtained reactivity ratios of the system AAM/DMAEA ($r_1 = 0.33$, $r_2 = 0.4$) from a solution copolymerization with a solid content of 5 wt%. Comparing the ultimate copolymerization model, fit using the reactivity ratios of Baade *et al.*[9], with our experimental results, significant differences are found as shown in *Figure 4*. Indeed, the trend in the experimental data is opposite to that of the prediction of the classical copolymerization model when the conversion is higher than 20%. The differences shown in *Figure 4* illustrate that the classical copolymerization model is not suitable for concentrated heterophase water-in-oil copolymerizations of ionogenic monomers. In particular, for industrial inverse-emulsion, inverse-suspension, or inverse-microemulsion copolymerizations with high monomer concentrations, the classical model, which uses the reactivity ratios as constants, will not give accurate predictions of the copolymer composition. If a copolymer composition control system is designed based on the prediction of the classical copolymer model, the lack of an accurate model will lead to an undesired composition drift.

Copolymerization is a very complex chemical reaction. There are several parameters influencing the copolymer composition, such as monomer concentration, pH, ionic strength, solvent type, and whether the reaction is

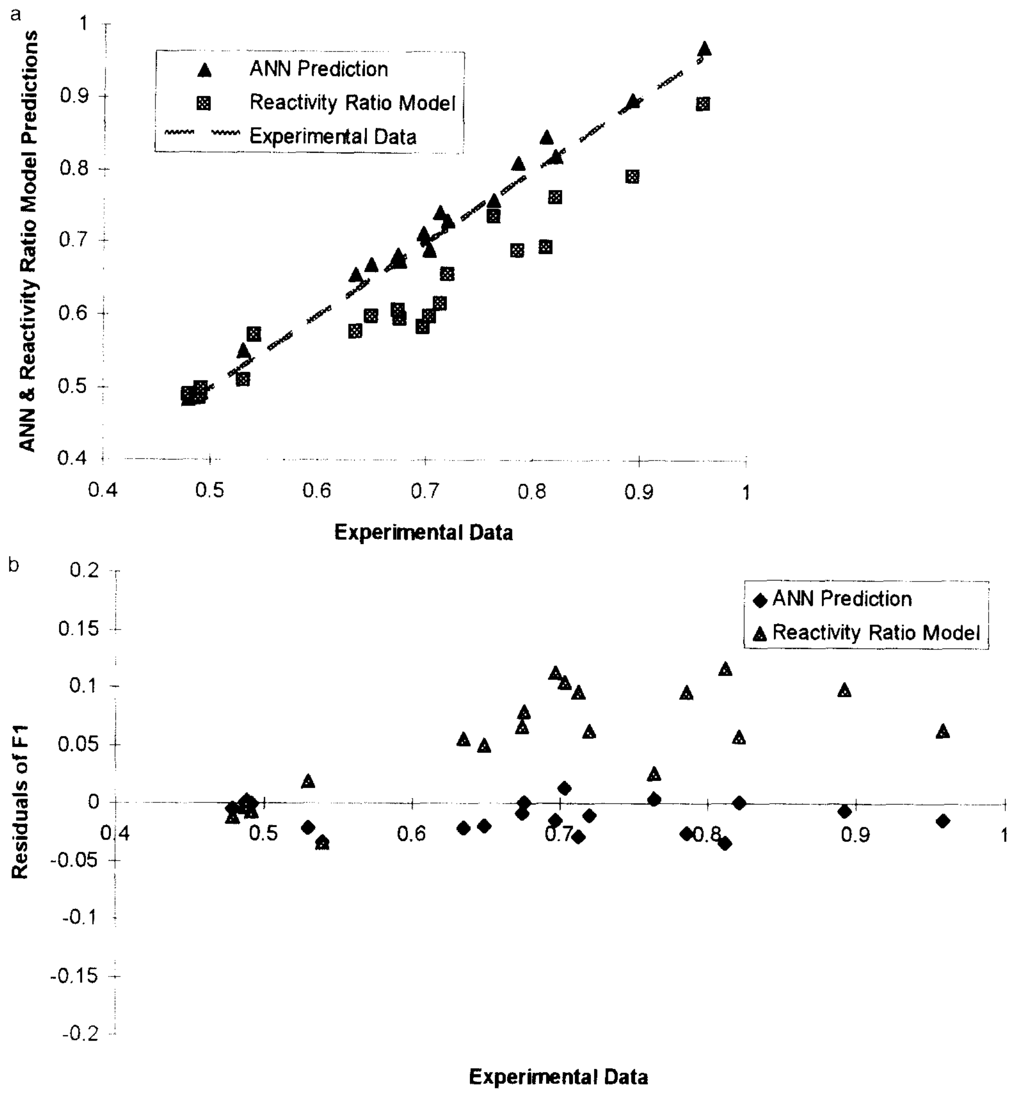

Figure 6 (a) A comparison of the predictibility of the ANN and the reactivity ratio models against experimental data to which the models were not fitted. (b) Residual (experimental–model prediction) for the ANN and reactivity ratio models. The same data were used as is shown in *Figure 6a*

carried out homogeneously or in a heterophase system. As mentioned in the Introduction, the alternative models which are based on mechanisms such as the penultimate group reactivity model, are composed of too many non-independent parameters to be of any practical use. Artificial neural networks (ANNs) have the ability to map nonlinear relationships without prior information about process or system models. One can take the copolymerization process as a 'grey' box, and train a neural network using experimental data, which were generated from copolymerization experiments under conditions similar to those of commercial production. In this work, the training data set includes 275 exemplars obtained from 11 copolymerizations under different reaction conditions shown in *Table 2*. For each reaction at least 15 samples were withdrawn as a function of conversion for monomer concentration determination. *Table 3* shows a partial list of the 275 exemplars. During the training process, the neurons learn the relationship between output variable (F_1) and input variables (monomer concentrations, polymer concentration, surfactant concentration and temperature) by adjusting the connection weights. *Figure 5* shows the learning profile during the training process. The error function ($E = 1/2\Sigma e_i^2$) decreases during the training process, where e_i is the error between experimental data and the ANN prediction of the ith exemplar. After the ANN has been trained, it can be used to predict copolymer composition at different conditions. From the weights of the well-trained neural network, we can find the importance of the various variables to the output (F_1). *Table 4* shows the connection weights in the input layer. It can be seen that all of the weights connecting the phase ratio R and surfactant concentration C_s in the input layer of the network are very small (less than 0.1). Therefore, phase ratio and surfactant concentration do not influence the copolymer composition significantly. However, the connection weights of the monomer concentrations, input variables C_1 and C_2, are very large relative to the other parameters. This indicates that the monomer feed ratio greatly influences the copolymer composition, as would be expected. The polymer concentration and reaction temperature also have a connection within the networks, and these two parameters slightly influence the copolymer composition. The polymer concentration effect is believed to have two contributing factors. A high viscosity macro-ion solution will influence the diffusion of the cationic functional group, whether on the free end of a chain or a macromolecule, in a non-equal manner, and thereby change the relative reactivities.

Table 5 Reaction conditions and the comparison of the copolymer composition between experimental data and the prediction of the ANN and reactivity ratio model[a]

C_1 (wt%) of the aqueous phase	C_2 (wt%) of the aqueous phase	C_p (wt%) of the aqueous phase	T (°C)	Phase ratio (aq. wt fraction)	F_1 Experimental	F_1 from ANN prediction	F_1 from the reactivity ratio model
22.8	15.4	11.8	35	0.5743	0.574	0.573	0.54
11.46	5.8	38.54	30	0.5743	0.635	0.656	0.579
8.745	4.3	36.96	30	0.5743	0.697	0.713	0.583
32.55	14.21	3	30	0.505	0.704	0.690	0.599
27.3	12.18	10.52	30	0.505	0.676	0.675	0.596
25.13	11.02	13.85	37	0.505	0.649	0.669	0.599
18.4	7.533	24.09	37	0.505	0.674	0.682	0.608
12.1	4.66	33.3	30	0.505	0.713	0.743	0.616
26.6	7.68	15.72	30	0.5	0.72	0.73	0.658
16.1	3.72	30.2	30	0.5	0.786	0.813	0.69
12.8	2.856	34.334	40	0.5	0.812	0.847	0.695
34.8	5.77	9.43	40	0.523	0.764	0.756	0.737
25.4	3.5	21.1	40	0.523	0.821	0.82	0.763
15.52	1.7	32.8	40	0.523	0.892	0.90	0.794
1.95	0.0845	48	40	0.523	0.958	0.972	0.894
25.0	25.0	0	35	0.6	0.489	0.493	0.487
20.5	20.1	9.375	35	0.6	0.487	0.487	0.49
18.2	17.65	14.2	35	0.6	0.479	0.484	0.491
14.75	13.475	21.78	35	0.6	0.491	0.493	0.499
8.75	7.325	33.925	35	0.6	0.53	0.552	0.511

[a] These data are plotted in *Figure 6a*

Furthermore, the charge on the end of a macro-ion chain may be screened by the charges of neighbouring polymer coils. Because the degree of interchain enlargements increases with conversion, this will influence the ionic atmosphere around the charged ultimate functional group. Clearly, the effect of polymer contribution is not normally considered nor is it necessary. However, it does appear to occur based on the data presented herein for the aqueous copolymerization of cationic monomers. That is, the polymer concentration dependence is likely due to the electrolytic nature of the macromolecule and reaction media. *Figure 6a* shows the comparison of copolymer compositions between untrained experimental data and the ANN prediction. The ANN predictions agree with the experimental data very well, while the reactivity ratio model has errors as high as 20%. It is important to note that the ANN was not trained with the data in *Figure 6*, and so the prediction of the ANN is therefore not merely curve fitting. *Figure 6b* plots the residues (experimental, model) for the ANN and the reactivity ratio scheme. The advantages of the ANN are clear. *Table 5* shows the reaction conditions and the copolymer composition comparison shown in *Figure 6*. All the data generated in *Table 5* represent additional experiments on which the ANN was not trained. *Figure 7* shows a typical comparison of copolymerization composition drift between experimental data and the ANN prediction as a function of the reaction conversion.

Implementation of the ANN for copolymer composition prediction

As mentioned above, the phase ratio (R) and the surfactant concentration (C_s) do not influence the copolymer composition and these two inputs were removed from the network. Therefore, the ANN developed herein consist of four input variables: C_1, C_2, C_p and T. The copolymer composition computing procedure developed herein consists of three steps: (1) precalculation, (2) ANN calculation and (3) post-calculation. In the first step, the input variables are normalized into the range (0, 10). C_1 = AAM weight fraction of the emulsion × 10; C_2 = DMAEA weight fraction × 10; C_p = polymer weight fraction × 10; T = *reaction* temperature (°C)/10. In the second step, the trained neural network maps the input vector x into the copolymer composition F_1 as follows

$$F_1 = N[x] \tag{3}$$

where N denotes a composite nonlinear matrix operator $x = [C_1, C_2, C_p, T, -1]^T$ (where -1 is the bias). For the ANN for copolymer composition prediction shown in *Figure 3*, the mapping $x \rightarrow F_1$ as in (3) can be represented as

$$F_1 = \Gamma\{W\Gamma[V\Gamma(Ux)]\} \tag{4}$$

where the internal mappings are

$$\Gamma(Ux) = y \tag{5}$$

$$\Gamma[Vy] = z \tag{6}$$

y and z are the output vectors of the input layer and the hidden layer. The operator Γ is a nonlinear diagonal operator with diagonal elements being identical sigmoid mapping functions defined as in *Figure 2b*. The values of connection weight matrix W, V and V of the copolymer composition prediction ANN are:

$$W = [-2.7, 0.396, 0.97, -0.07, -0.963, -0.164, 1.6, 1.28, -1.42, -0.83, -0.49]^T \tag{7}$$

$$V = \begin{bmatrix} 1.233 & -1.975 & -0.782 & -1.122 & -0.209 & -1.976 & -0.619 \\ -0.234 & 0.191 & 0.285 & 0.222 & 0.065 & 0.094 & -0.053 \\ -0.824 & 0.314 & 0.389 & 0.448 & -0.102 & 0.444 & -0.145 \\ -0.02 & -0.246 & -0.074 & -0.019 & 0.079 & -0.032 & 0.002 \\ 0.913 & -0.306 & -0.289 & -0.314 & -0.138 & -0.314 & 0.154 \\ 0.276 & 0.03 & 0.117 & 0.143 & 0.124 & -0.345 & -0.046 \\ -1.326 & 0.436 & 0.971 & 0.498 & 0.232 & 0.441 & -0.256 \\ -1.146 & 0.569 & 0.578 & 0.471 & 0.405 & 0.199 & -0.085 \\ 1.359 & -0.132 & -0.582 & -0.535 & -0.065 & -0.690 & 0.053 \\ 0.953 & -0.081 & -0.129 & -0.215 & -0.135 & -0.206 & 0.068 \end{bmatrix} \qquad (8)$$

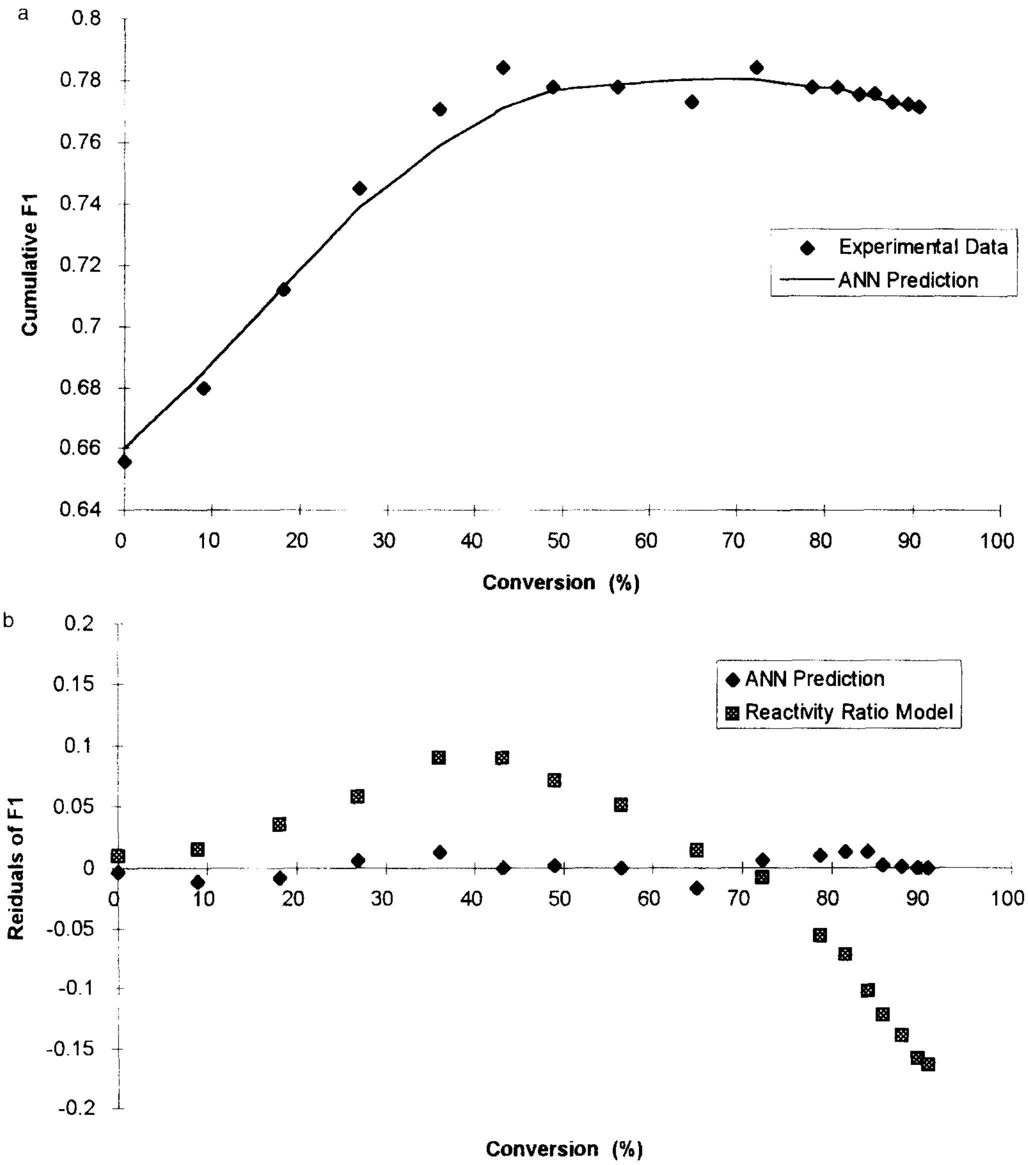

Figure 7 (a) Comparison of the predicted cumulative copolymer composition from the ANN and experimental data for a copolymerization of AAM and DMAEA. The following conditions were used: $[\mathrm{AAM}]^0 = 380\,\mathrm{g\,L_w^{-1}}$, $[\mathrm{DMAEA}]^0 = 120\,\mathrm{g\,L_w^{-1}}$, $T = 40^\circ\mathrm{C}$, aqueous-to-organic phase ratio = 1 : 1, [surfactant] = 4 wt% and an agitation rate of 400 r.p.m. (b) Residuals of the predicted copolymer composition of the ANN and reactivity rato model based on the data in *Figure 7a*

$$U = \begin{bmatrix} -3.661 & 0.714 & 0.049 & -0.229 & 0.365 \\ -1.359 & -1.638 & 0.046 & 0.11 & 0.624 \\ 1.462 & -1.213 & -0.228 & 0.071 & 0.9 \\ -0.648 & -1.337 & 0.153 & 0.072 & 0.095 \\ -0.15 & 0.389 & -0.082 & 0.019 & 0.032 \\ -0.28 & -2.106 & 0.233 & 0.101 & 0.633 \end{bmatrix} \tag{9}$$

The copolymer composition F_1^{ANN} can be computed from the input vector $\boldsymbol{x}$ using the mapping equation (4) with the connection weight matrix W, V and U. During the training process, the value of F_1^{ANN} was based on weight fraction. Therefore, the ANN output is the copolymer composition based on weight fraction. In the third step, the task of postcalculation is to convert the copolymer composition to the F_1 based on mole fraction. The formula is:

$$F_1 = \frac{F_1^{\text{ANN}}}{F_1^{\text{ANN}} + (1 - F_1^{\text{ANN}})\frac{M_1}{M_2}} \tag{10}$$

where M_1 and M_2 are the molecular weights of AAM and DMAEM, which are 71 and 196 respectively.

CONCLUSIONS

For the copolymerization of acrylamide with a quaternized cationic comonomer the reactivity ratios are conversion dependent. The classical binary ultimate reactivity copolymerization model which takes reactivity ratios as constants during the whole copolymerization reaction cannot give precise predictions of the copolymer composition. However, artificial neural networks have been shown to have advantages over the classical reactivity ratio model for copolymerization of AAM and electrolytic monomers. We expect that for any system when reactivity ratios change with conversion that an ANN scheme such as the one developed herein will be preferable.

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