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Copolymer Composition in High Pressure Copolymerizations of Ethylene with Vinyl Monomers*

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Summary

In the high pressure copolymerizations of ethylene with some vinyl monomers, the variation of the copolymer composition was calculated for two limiting types of flow models in reactor; Piston Flow (P.F.) and Complete Mixing Flow (C.M.). The arithmetical mean values of 2-dimethylaminoethyl methacrylate, styrene and glycidyl methacrylate contents in the respective copolymers of P.F. and C.M. models were in good agreement with the experimental results.

Introduction

Various copolymers of ethylene with vinyl monomers are produced commercially in continuous high pressure processes. In order to control the copolymer composition, the reaction conditions are set on the basis of the results obtained in a series of experiments by the batch-wise operations in a small size autoclave. Essential parameters for the copolymer compositions are the amount of vinyl monomer in feed and the conversions of ethylene and vinyl monomer. It is preferred, however, to predict the copolymer composition produced in continuous flow process. The present

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study deals with the calculation for the variations of the copolymer composition with the feed composition and with ethylene conversion. The calculated values have shown good agreement with the experimental results.

Experimental

Copolymerization was carried out in a batch-wise operation in a constant volume system using an autoclave (260 ml) with an inner stirrer. After the prescribed time, unreacted ethylene and vinyl monomer were released. The copolymers obtained were dissolved in hot xylene, and precipitated in methanol.

Analysis of vinyl monomer contents in copolymer were performed by elemental analysis for 2-dimethylaminoethyl methacrylate (DAM), and IR for styrene (ST) and glycidyl methacrylate (GMA). Calibration of IR spectra for ST was made with polyethylene-polystyrene-composed materials, and for GMA with the copolymers in xylene solution by titrating with HCl-Sodium methylate.

Results & Discussion

The basic differential equation which governs the composition of the copolymer is

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_1]}{[M_2] + r_2[M_2]} \qquad (1)$$

, where $[M_1]$ and $[M_2]$ are the molar concentrations of ethylene and vinyl monomers, respectively, and r_1 and r_2 are the monomer reactivity ratios (ALFREY et al. 1952). The Q- and e-values for ethylene, based on copolymerizations with n-butyl acrylate, vinyl acetate and vinyl chloride, were found to be 0.03 and -0.43, respectively (BURKHART & ZUTTY 1963). Monomer reactivity ratios were computed from the Q- and e-values for vinyl monomers of DAM, ST and GMA (Table 1)(YOUNG

1961).

TABLE 1

Monomer reactivity ratios calculated from Q- and e-values

Comonomers, M_2	Q	e	Monomer reactivity ratios r_1	r_2
DAM	0.68	0.48	0.03	14.7
ST	-0.80	1.00	0.04	24.8
GMA	0.85	0.10	0.03	26.9

Monomer M_1 : Ethylene, Q; 0.03, e; -0.43

a) Q- & e- values for GMA: From the technical information of " Blemmer G ", Nippon Oil & Fats Co., Ltd.

Typical limiting types of flow in continuous flow reactors are classified into two models, Piston Flow (P.F.) and Complete Mixing Flow(C.M.)(NAGATA 1975). In the P.F. model, reaction mixtures move in the direction of flow in reactor at a constant speed, and the mixing and diffusion in the flow are negligible. The C.M. model designates another limiting flow in which reaction mixtures are in complete mixing condition at any part of reactor and the effluent from reactor is also in the same compositions as that in reactor. In actual flow reactors, an intermediate type of flow between these two extremes is assumed to take place.

For each flow models, the calculations for the variations of the copolymer composition with the feed composition and with the ethylene conversion were performed by a computer using Fortran program (Programing Language FORTRAN(level 7000), JIS 6201-1976). Some results of calculations are shown in Figures 1 and 2.

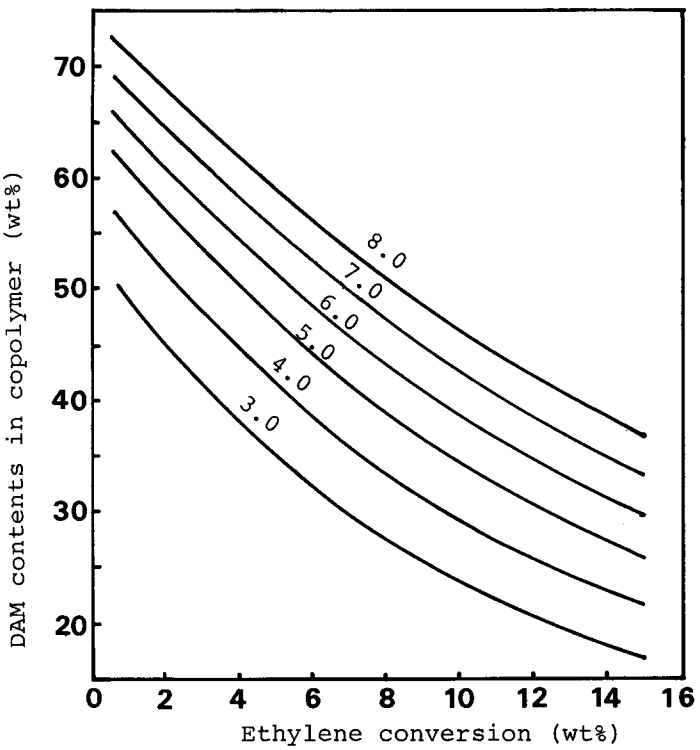

Fig. 1 Relationship between ethylene conv. and DAM conts. Calculation for complete mixing model. Numerals in the Figure are the DAM wt% in gas feed.

The calculated values were compared with the experimental results which were obtained in a series of batch-wise experiments. Experimental results of the ethylene-DAM copolymerization are shown in Table 2 and Figure 3. Table 3 and 4 show that the arithmetical mean values of DAM contents in copolymers of P.F. and C.M. models are in good agreement with the experimental results. In the copolymerizations with ST and with GMA, excellent agreements between the calculated values and observed values have also been demonstrated (Tables 5 and 6).

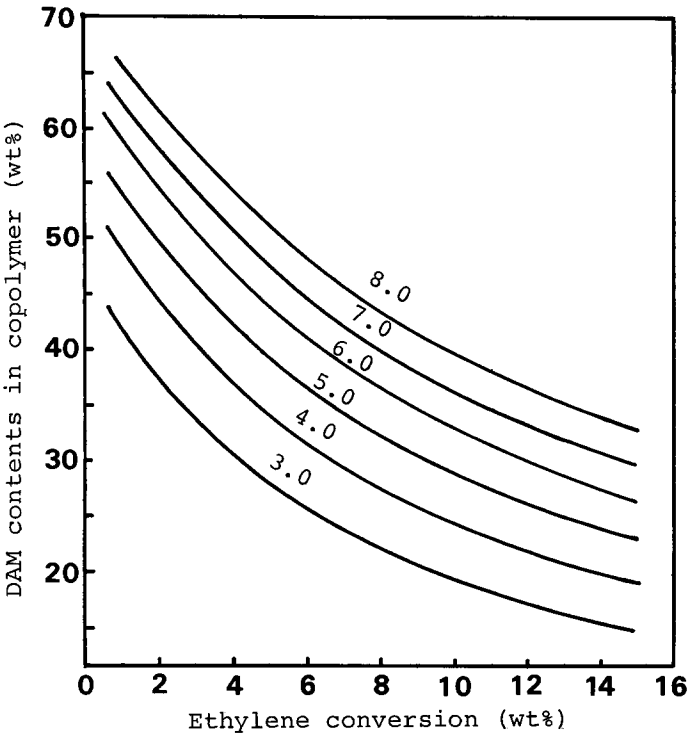

Fig. 2 Relationship between ethylene conv. and DAM conts. Calculation for piston flow model. Numerals in the Figure are the DAM wt% in gas feed.

TABLE 2

High pressure copolymerization of ethylene with DAM in batch.

DAM wt% in gas feed	Press. (kg/cm^2)	Temp. (°C)	Yield (g)	DAM conts.[a] (wt%)	Conv. DAM (wt%)	Conv. E[b] (wt%)
5.1	1530	152	17.8	34.0	87.2	9.1
5.0	1510	149-157	21.0	30.2	91.0	11.2
5.0	1540	160-175	22.4	28.1	90.3	12.3
5.0	1600	144-155	9.3	52.7	70.8	3.3
5.0	1485	151	16.7	33.5	80.3	8.5

a) Elemental analysis, b) Ethylene

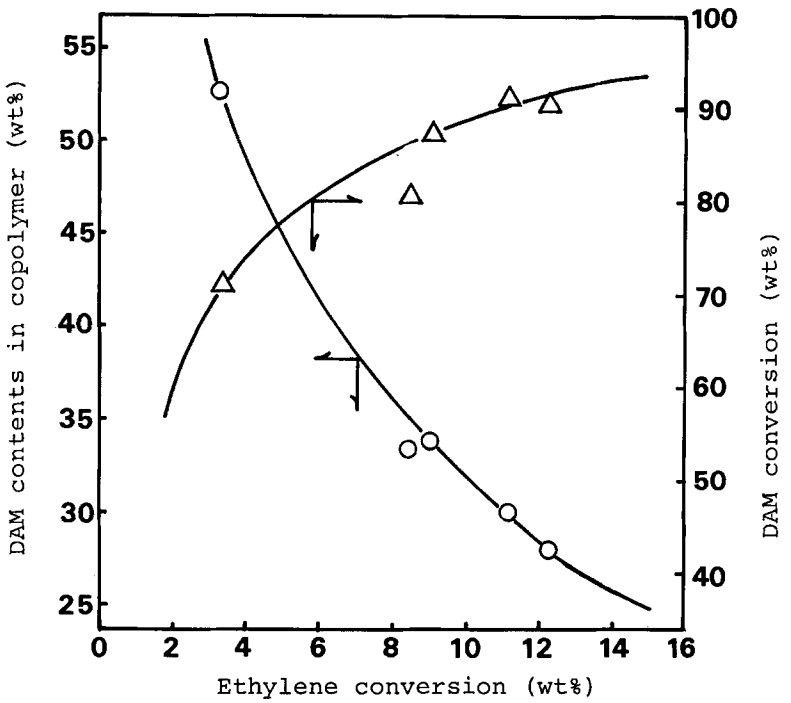

Fig. 3 Relationship between ethylene conv. and DAM conts. in batch-wise copolymerization. DAM in gas feed: 5 wt%.

TABLE 3

Ethylene-DAM copolymerization. Comparison between calculated values and experimental results of copolymer composition (DAM in gas feed: 5 wt%).

Ethylene conv.(wt%)	10.0	11.0	12.0	13.0	14.0	15.0
DAM conts.(wt%) (Calculated)						
P.F. (I)	34.1	32.1	30.3	28.8	27.7	26.0
C.M. (II)	29.1	27.7	26.3	25.1	24.0	23.0
Av. values[a)]	32	30	28	27	26	25
Observed values[b)]	32	30	29	28	26	25

a) Arithmetical means of (I) & (II).

b) From the values of Figure 3.

Table 4

Ethylene-DAM copolymerization. Comparison between the calculated and observed values of DAM conversion at varied conversions of ethylene (DAM in gas feed: 5 wt%).

Ethylene conv.(wt%)	10.0	11.0	12.0	13.0	14.0	15.0
DAM conv.(wt%) (Calculated)						
P.F. (I)	98.7	98.9	99.3	99.6	99.7	99.8
C.M. (II)	78.0	79.9	81.4	82.8	84.0	85.1
Av. values[a)]	88	89	90	91	92	93
Observed values[b)]	89	90	90	92	93	93

a) Arithmetical means of (I) & (II).

b) From the values of Figure 3.

Table 5

Ethylene-ST copolymerization. Comparison between the calculated and observed values of ST content at varied conversion of ethylene.

ST wt% in gas feed	2.0	2.0	2.0	4.0
Ethylene conversion (wt%)	3.0	4.0	5.0	6.0
ST contents(wt%) (Calculated)				
P.F. (I)	28.4	26.3	23.9	22.0
C.M. (II)	22.9	20.7	18.8	17.3
Av. values[a)]	26	24	22	20
Observed values[b)]	30	26	23	22

a) Arithmetical means of (I) & (II).

b) From the results of batch-wise synthesis.

TABLE 6

Ethylene-GMA copolymerization. Comparison between the calculated and observed values of GMA content at varied ethylene conversions.

GMA wt% in gas feed	1.7	1.7	1.7	4.1	4.1
Ethylene conv.(wt%)	7.0	8.0	9.0	5.0	10.0
GMA conts.(wt%) (Calculated)					
P.F. (I)	19.7	17.7	16.1	45.0	29.9
C.M. (II)	16.3	14.9	13.7	37.8	26.5
Av. values[a)]	18	16	15	41	28
Observed values[b)]	17	16	14	37	28

a) Arithmetical means of (I) & (II).

b) From the results of batch-wise synthesis.

Now the calculation method described here has been found valid for predicting the composition of copolymer in high pressure copolymerization of ethylene.

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