Specific Surface Prediction through Copolymerization Kinetic Modeling

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INTRODUCTION

Polymer-supported catalysts represent an environmentally friendly alternative in comparison with metal catalysts. Furthermore, polymer gels with desirable properties (e.g., porosity, specific surface) can be designed through varying polymerization conditions and feeding concentrations[1,2]. Most literature copolymerization models give predictions on species concentrations, monomer conversion and molecular weight distribution. On the other hand, structural aspects such as specific surface are not taken into account. Since this property is of utmost importance in catalysis application, a kinetic modeling able to predict specific surface of gel particles during copolymerization was developed by the present research group[3]. The present work shows the model validation with experimental data obtained in laboratory.

METHODOLOGY

Suspension (15% organic 85% aqueous in volume) copolymerizations of styrene with ethylene glycol dimethacrylate (EGDMA) in presence of toluene and heptane were carried out in batch reactor of 1 L during 6 h at 80°C. Benzoyl peroxide was used as initiator (1%) and polyvinyl alcohol was used as dispersing agent (1%). Table 1 shows the feeding conditions.

Table 1 – Feeding.

Run	Y_{dma}	Y_{tol}
1	0.1	0.4
2	0.3	0.5
3	0.5	0.6

Y_{tol} is the volumetric fraction of toluene in the solvents mixture. Y_{DMA} is the molar fraction of EGDMA in the monomer mixture. Organic phase was composed of 30% monomers and 70% solvents.

The mathematical model was based on molar balances, method of moments and numerical fractionation[3]. The specific surface area (SA) was calculated through eq. 1.

$$SA = \frac{GN_A\left(4\pi R_g^2\right)}{10^{18} W_g Q_1 \overline{M_M}} \qquad (1)$$

Where G: concentration of elementary gel structures (EGS), N_A: Avogadro number, R_g: estimated EGS radius of gyration, W_g: weight fraction of gel, Q_1: concentration of monomer units, M_M: monomer molecular weight.

RESULTS AND DISCUSSION

Fig. 1 presents a comparison between experimental results of specific surface and model predictions.

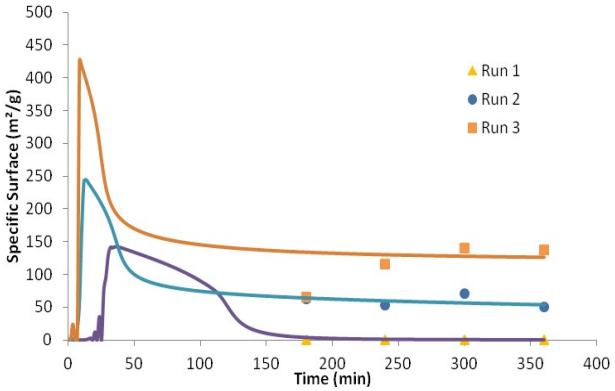

Fig. 1 – Experimental and model results. Dots: experimental, Lines: Model. α= 0,368 (Run 1), α= 0,387 (Run 2), α= 0,406 (Run 3).

The parameter α is an apparent coiling factor for the gel molecules after drying. For unperturbed chains, this factor is 0.5. After drying process, it is expected lower values due to chain grouping (see captions of Fig 1). The fitted α values are directly proportional EGDMA dosages, suggesting that higher surface areas are obtained when higher heterogeneity is caused in the medium.

CONCLUSION

A mathematical model for prediction of copolymer gels specific surface was developed and validated with experimental data. The model proved predictive for the conditions studied and can be extended to other copolymerization systems with gel formation.

REFERENCES

[1] K. A. Kun et al. J. Polym. Sci (Chem), 6, 2689 (1968).
[2] A. Nodehi et al. J. App. Polym. Sci. 120, 1942-1949 (2011).
[3] L. G. Aguiar Macromol. React. Eng 10, 588-599 (2016).

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