

concentration of $\text{Mo}(\text{CO})_6$ increases, but that the number of chains formed will be proportional to $[\text{Mo}(\text{CO})_6]_0$. Assuming the same dependence of chain length on rate of initiation as in homogeneous systems we predict that the yield of graft polymer will be proportional to $[\text{Mo}(\text{CO})_6]_0^{1/2}$.

At high $[\text{Mo}(\text{CO})_6]_0$ ($\sim 10^{-2} \text{ mol l}^{-1}$) rates of initiation will be high with high local concentrations of propagating radicals on the surfaces. Mutual termination of these radicals will result in comparatively short grafts. It is also likely that, under the reaction conditions employed, the surface will become effectively saturated with interpenetrating grafts forming a barrier to further reaction. Thus, a constant number of grafts may be formed. Their average length and, hence, the polymer yield will decrease with increasing $[\text{Mo}(\text{CO})_6]_0$.

DISCUSSION

The analytical and spectroscopic data demonstrate that we have developed a successful method of incorporating on to glass surfaces reactive groups which can act as initiation sites for graft polymerization in the presence of molybdenum carbonyl and suitable monomer. Quantitative data and the results of electron microscopy are consistent with the formation of an essentially uniform 'monomolecular' layer of grafts on the glass surface.

Under the conditions of our experiments we expect approximately three hydroxyl groups per 1 nm^2 of the glass surface¹⁵ to be available for chlorination. Assuming one third of these sites eventually become points of attachment of graft chains there would be, on average, about one junction point per 100 \AA^2 . For a polymer layer 0.25 \mu m thick (see Table 2), these conditions correspond to a degree of polymerization of about 1000 per graft site, which is a sensible kinetic chain length for free-radical polymerization. Because of the modes of bimolecular termination of propagating radicals¹⁶ PMMA is expected to form mainly simple grafts while, depending on the extent of transfer and thermal initiation, a large proportion of the PSt chains are expected to be in the form of loops on the glass surface.

Currently, work is in progress to determine the numbers and lengths of the grafts and to develop reproducible methods of incorporating grafted beads into polymeric matrices where it is highly probable that at equilibrium the mixing of bound and unbound chains is unfavourable^{17,18}

Kinetics of cure of epoxy resin system bisphenol-A diglycidylether-di(4-aminophenyl)sulphone

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Introduction

In this communication, the kinetics of cure of stoichiometric mixtures of the epoxy resin bisphenol-A diglycidylether, and the curing agent di(4-aminophenyl)sulphone, have been investigated by differential scanning calorimetry in the temperature range $140^\circ\text{--}200^\circ\text{C}$. The results are described by a kinetic equation which accounts for the diffusion control of the curing reactions. It is assumed that the rate-determining step is the autocatalysed reaction of an epoxide-amine complex with hydrogen-bond donor mole-

Only then will it be possible to control the interfaces between grafted beads and a matrix.

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References

- 1 Nielsen, L. E. *J. Appl. Polym. Sci.*, 1966, **10**, 97
- 2 Morton, M., Murphy, R. J. and Cheng, T. C. in 'Copolymers, Polyblends and Composites' (Ed. N. A. J. Platzer) *Adv. Chem. Ser.* **142**, Am. Chem. Soc., 1975
- 3 Lewis, T. B. and Nielsen, L. E. *J. Appl. Polym. Sci.* 1970, **14**, 1449
- 4 For example, Kaas, R. L. and Kardos, J. L. *Polym. Eng. Sci.* 1971, **11**, 11
- 5 Hair, M. L. 'Infrared Spectroscopy in Surface Chemistry', Marcel Dekker, NY, 1967; Elmer, T. H. and Nordberg, M. E. Belg. Pat. 650,244 (1965)
- 6 Deuel, H., Wartmann, J., Hutschnecker, K., Scholinger, U. and Güdel, C. *Helv. Chim. Acta* 1959, **42**, 1160
- 7 Folman, M. *Trans. Faraday Soc.* 1967, **57**, 2000; Scherbakova and Slovetskaya, *Dokl. Akad. Sci. USSR* 1951, **111**, 855
- 8 Buslaev, G. S., Karitonov, N. P. and Platonova, V. I. *Izv. Akad. Nauk SSSR, Neorgan Materialy*, 1965, **1**, 1607
- 9 Beachell, H. C. *J. Am. Chem. Soc.* 1952, **74**, 5247
- 10 Bamford, C. H., Eastmond, G. C. and Maltman, W. R. *Trans. Faraday Soc.* 1966, **62**, 2531
- 11 Bamford, C. H., Eastmond, G. C. and Fildes, F. J. T. *Proc. Roy. Soc.*, 1972, **A326**, 431
- 12 Bamford, C. H., Dyson, R. W., Eastmond, G. C. and Whittle, D. *Polymer* 1964, **10**, 759
- 13 Bamford, C. H. and Sakamoto, I. *J. Chem. Soc. Faraday Trans. I* 1974, **70**, 344
- 14 Bamford, C. H., Denyer, R. and Eastmond, G. C. *Trans. Faraday Soc.* 1965, **61**, 1459
- 15 Dawson, J. B. Pilkington Bros. Ltd, private communication
- 16 Bamford, C. H., Dyson, R. W. and Eastmond, G. C. *Polymer* 1969, **10**, 885
- 17 Eastmond, G. C. and Phillips, D. G. in 'Polymer Alloys' (Eds. D. Klempner and K. C. Frisch) Plenum Press, NY 1977, 141; *Polymer* 1979, **20**, 1501
- 18 Meier, D. J. *Polym. Prepr.* 1977, **18**(1), 340

cules, such as species containing hydroxyl groups.

A common feature of many epoxy resin systems is that the curing process is autocatalytic in nature and is diffusion-controlled in its later stages. A quantitative description of the curing process should account for these phenomena.

A kinetic equation which has been used to describe the autocatalytic cure of various epoxy resin systems is of the form:

$$r = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (1)$$

where α is the fractional degree of conversion, the rate $r = d\alpha/dt$, k_1 and k_2 are temperature dependent constants, and m and n are constants¹⁻³. Horie *et al.*¹ derived equation (1) with $m = 1$, $n = 2$, from a proposed kinetic mechanism for the addition of stoichiometric proportions of primary or secondary amines to epoxides. The generation of catalytic hydroxyl groups by the amine-epoxide addition explained the autocatalytic features of the overall reaction. Following Smith⁴, the rate determining step was assumed to be the termolecular reaction of amine, epoxide, and hydrogen-bond donor molecules.

For aliphatic diamines, the model gave good fits to the experimental isothermal rate data up to about 50–70% conversion, above which a sharp deceleration in rate was observed and attributed to the onset of diffusion control. Sourour and Kamal² applied the same model to isothermal rate data for the cure of bisphenol-A diglycidyl ether resin with *m*-phenylene diamine and obtained good fits to the data in the 40–60% conversion range, with a similar retardation at higher conversions.

If the rate determining step is assumed to be the autocatalysed reaction of a rapidly formed complex of epoxide and amine, then the resulting kinetic expression is equation (1) with $m = n = 1$. Enikolopiyan⁵ has presented some evidence that such complex formation does occur, so that this form of equation (1) provides another possible model for the cure kinetics.

A disadvantage of equation (1) is that it cannot account for the observed retardation with increasing conversion, and for the limited conversions observed at temperatures lower than the glass transition temperature (T_g) of the fully cured material.

There is evidence that the rate coefficients for diffusion controlled reactions are inversely proportional to the viscosity of the reaction medium⁶. For epoxy-amine cure, the critical gel point conversion has been found to be constant even when cure occurred above the T_g of the system, implying that all the reaction steps were retarded to the same degree for a given increase in viscosity⁷.

If the retardation in rate with conversion is assumed to be due to the increase in viscosity as the resin gels and cross-links, and if, as a first approximation, the rate parameters k_1 and k_2 are assumed to decrease linearly with increasing conversion, then equation (1) can be written in the modified form:

$$r = (k'_1 + k'_2\alpha^m)(1 - \alpha)^n \quad (2)$$

The retarded rate parameters are given by $k'_1 = (k_1 - s_1\alpha)$, $k'_2 = (k_2 - s_2\alpha)$, where the constants s_1 and s_2 are $s_1 = -dk'_1/d\alpha$, $s_2 = -dk'_2/d\alpha$. If k'_1 and k'_2 are zero at the same limiting value of conversion, then, for a given temperature and conversion, the ratio $k_1/k_2 = k'_1/k'_2$. For $m = 1$, equation (2) can be written as:

$$r = (A_0 + A_1\alpha + A_2\alpha^2)(1 - \alpha)^n \quad (3)$$

where $A_0 = k_1$, $A_1 = k_2 - s_1$, $A_2 = -s_2$.

The model thus predicts that $r/(1 - \alpha)^n$ should be a quadratic function of α , when $m = 1$.

Experimental

Materials. The resin was Shell Epikote 828 with an epoxide value of 5.21 equivalents kg^{-1} . The di(4-amino-

phenyl)sulphone was Koch-Light purissimum grade.

Differential scanning calorimetry (d.s.c.). The instrument was the Du Pont Thermal Analyser with d.s.c. cell, operated with a nitrogen flow of about $30 \text{ cm}^3 \text{ min}^{-1}$ through the cell. The heat flow and temperature signals were measured with a digital voltmeter and recorded on punched tape for computer processing. A pure alumina disc was used as the enthalpy standard for the calorimetric calibration of the instrument.

The resin formulations were prepared in batches of about 2 g by mixing in a glass tube at $135^\circ \pm 1^\circ \text{C}$ for 15 min to obtain complete solution. Samples of the resin (5–40 mg) were weighed accurately in open aluminium pans and cured in the d.s.c. at constant heating rate or under isothermal conditions. For isothermal measurements, the instrument was first equilibrated at the required temperature and then the sample pan was inserted. Thermal equilibrium was regained within 1–2 min after insertion of the sample. T_g of the cured resins were determined from d.s.c. scans at 20 K min^{-1} heating rate. T_g was taken to be the inflection in the heat flow-temperature curve in the region of discontinuity in heat capacity.

The d.s.c. output data were processed by computer to give heat flow, dq/dt , as a function of temperature and time. Between the limits of the cure exotherm for experiments at constant heating rate a linear baseline was assumed, and the total heat of reaction, q_0 , was found by trapezoidal integration of the heat flow/time data. For isothermal experiments, the baseline was obtained by horizontal extrapolation of the final five heat flow data points, after the reaction had essentially stopped, to intersect with the initial onset of the reaction exotherm. This intersection was taken as the zero time of the reaction. At a given time, the extent of reaction, α , was obtained from the ratio, q_t/q_0 , of the partial heat of reaction at that time to the total heat of reaction found from the constant heating rate experiments.

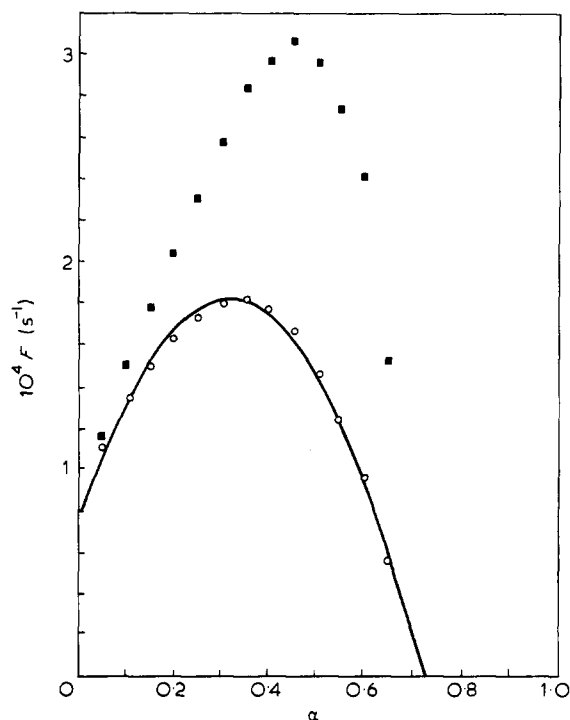


Figure 1 Kinetic data at 142°C . Plot of the rate function $F = r/(1 - \alpha)^n$ against conversion. \circ , $n = 1$; \blacksquare , $n = 2$; —, quadratic regression curve for equation (3)

Table 1 Isothermal cure

Temperature (°C)	q_T (J g ⁻¹)	α	T_g (°C)
142	220.1	0.68	—
161	243.5	0.75	138
180	307.7	0.95	168
190	322.8	0.99	183
200	329.5	1.02	189

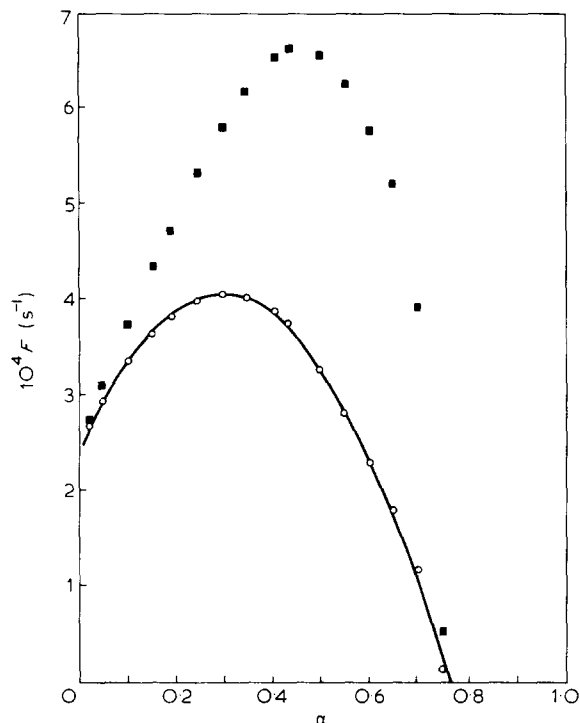


Figure 2 Kinetic data at 161°C. Symbols and line as in Figure 1

Results and discussion

The total heat of cure, q_0 , was found from four d.s.c. scans at heating rates of 1, 5 or 10K min⁻¹, by numerical integration of the heat flow–time data. The value obtained for q_0 was 324.5 J g⁻¹, and the standard deviation was 25.4 J g⁻¹.

Isothermal cure data were obtained in the range 142°–200°C. The apparent heat of cure, q_T , conversion, $\alpha = q_T/q_0$, and T_g values are shown in Table 1.

A test of equation (1) with $m = 1$ as an expression for the isothermal cure kinetics is provided by plots of the reduced rate, $r/(1 - \alpha)^n$, against α . The plots should be linear if equation (1) is applicable. The isothermal data are plotted in this form in Figures 1–5 and it appears that equation (1) does not provide a good description of the data over a wide range of conversion. In the case of $n = 2$, the curves are approximately linear at low degrees of conversion. For $n = 1$, the curves consistently show a retardation in the reduced rate with increasing conversion.

The proposed rate expression allowing for diffusion control, equation (3), predicts that $r/(1 - \alpha)$ should be a quadratic function of α , if $n = 1$. The isothermal data were subjected to a quadratic least squares regression analysis and the resulting regression curves are shown in Figures 1–5. The data do not conform exactly to the quadratic function, and deviations are especially obvious at the higher temperatures. This is probably due to the inaccuracy of the assumption that k_1 and k_2 are simply inversely dependent on conversion, or that the parameters m and n are exactly equal

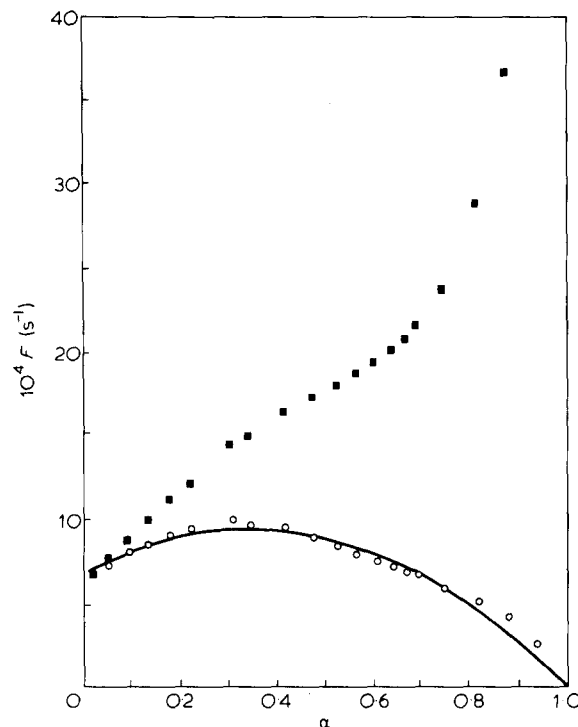


Figure 3 Kinetic data at 180°C. Symbols and line as in Figure 1

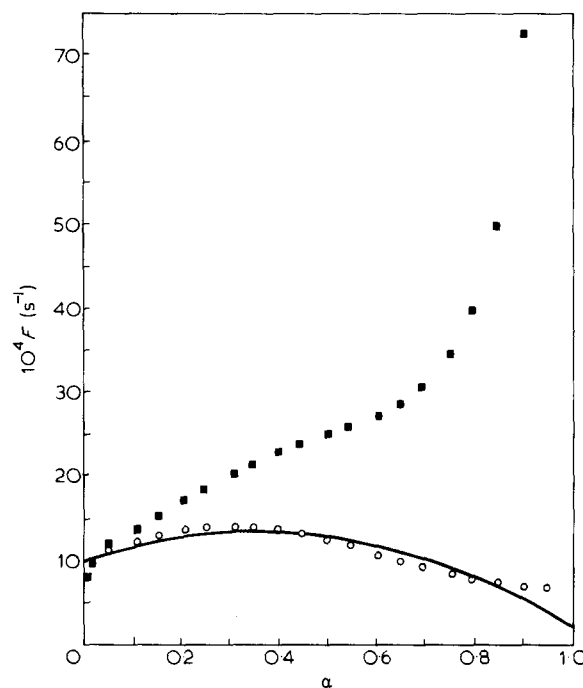


Figure 4 Kinetic data at 190°C. Symbols and line as in Figure 1

to 1. However the proposed model does provide a useful approximation to the observed data.

The coefficients A_i of equation (3) are correlated with temperature to a good approximation by the Arrhenius relationship:

$$A_i = \exp(B_i - C_i/RT) \quad (4)$$

where T is the temperature (K). The plots of $\ln A_i$ against reciprocal absolute temperature are shown in Figure 6, and the values of B_i and C_i from linear regression are given in Table 2.

Table 2 Values of B_i and C_i in equation (4)

i	B_i	C_i
0	15.222	10 247.24
1	2.568	4080.77
2	1.745	3534.08

Table 3 Values of the kinetic parameters

Temperature (°C)	$10^4 k_1$ s ⁻¹	$10^4 k_2$ s ⁻¹	s_1 s ⁻¹	s_2 s ⁻¹
142	0.73	7.91	1.00	10.91
161	2.38	14.26	3.11	18.61
180	6.74	21.96	6.73	21.91
190	9.72	29.19	9.14	27.43
200	14.96	36.64	13.48	33.03

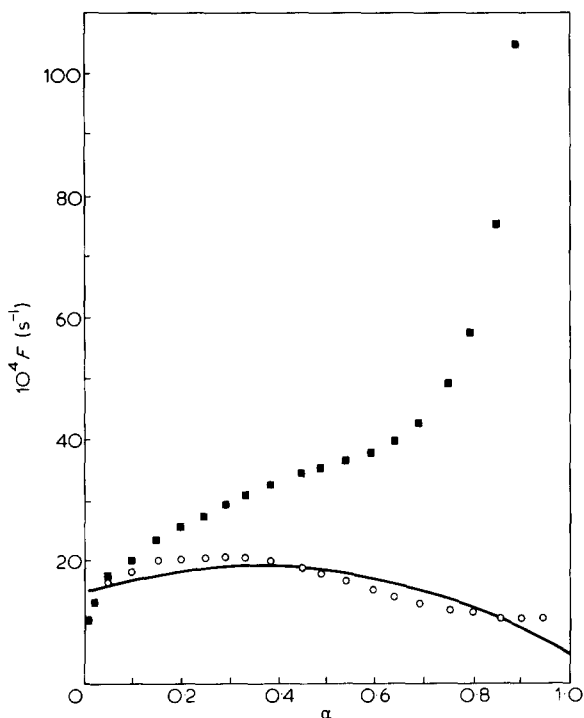


Figure 5 Kinetic data at 200°C. Symbols and line as in Figure 1

The values found for the kinetic parameters k_1, k_2, s_1 and s_2 are given in Table 3.

The apparent activation energy for k_1 and k_2 is 85.3 and 42.8 kJ mol⁻¹, respectively. These values are close to those found by Sourour and Kamal² for a similar resin cured by *m*-phenylene diamine, 88.2 and 46.0 kJ mol⁻¹, respectively. In this case the data were fitted to equation (1) at low conversion, for $m = 1$ and $n = 2$.

Values of time to reach a given conversion at a given temperature can be found by numerical integration of equation (3), with $n = 1$:

$$\int_0^\alpha \frac{d\alpha}{(A_0 + A_1\alpha + A_2\alpha^2)(1 - \alpha)} = t_\alpha \quad (5)$$

The calculation was done at each experimental temperature, using the Arrhenius parameters of Table 2 to calculate A_0, A_1 and A_2 . Trapezoidal integration was used for incre-

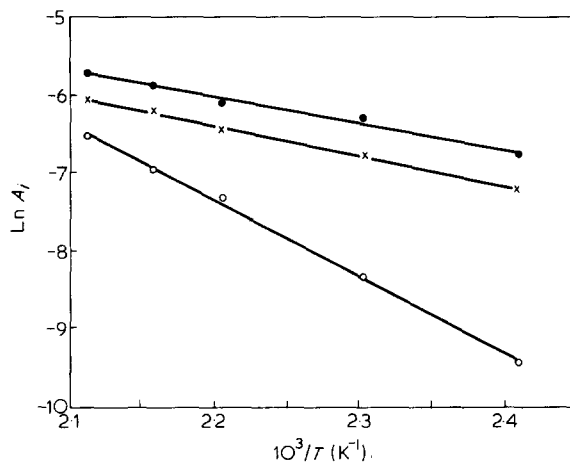


Figure 6 Plots of $\ln A_i$ against reciprocal temperature. $\circ, i = 0$; $\times, i = 1$; $\bullet, i = 2$

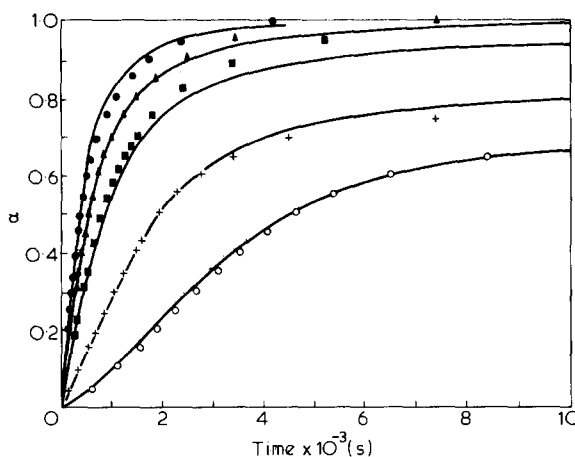


Figure 7 Isothermal conversion-time data. $\circ, 142^\circ$; $\times, 161^\circ$; $\blacksquare, 180^\circ$; $\blacktriangle, 190^\circ$; $\bullet, 200^\circ$ C. Solid curves are calculated from equation (5)

ments in α of 0.01. The quite good agreement between the experimental data and the calculated curves is illustrated by Figure 7.

Conclusions

The isothermal cure kinetics of the resin system show features of autocatalysis and diffusion control similar to those observed for other aliphatic and aromatic diamine curing agents. A modified kinetic equation is proposed which accounts for the diffusion control of the curing reaction. Although the model is based on the simple assumption that the rate coefficients are inversely proportional to the extent of reaction, it does provide a reasonable and useful fit to the experimental data.

References

- Horie, K., Hiura, H., Sawada, M., Mita, I. and Kambe, K. *J. Polym. Sci. A-1* 1970, 8, 1357
- Sourour, S. and Kamal, M. R. *Thermochim. Acta* 1976, 14, 41
- Ryan, M. E. and Dutta, A. *Polymer* 1979, 20, 203
- Smith, I. T. *Polymer* 1961, 2, 95
- Enikolopiyan, N. S. *Pure Appl. Chem.* 1976, 48, 317
- Allen, P. E. M. and Patrick, C. R. 'Kinetics and mechanisms of polymerization reactions', Ellis Horwood, Chichester, 1974, Ch. 2
- Lunak, S., Vladyka, J. and Dusek, K. *Polymer* 1978, 19, 931

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