Solid state polymerization of N-substituted acrylamides: 2

J. Żurakowska-Orszàgh
Department of Chemistry, University of Warsaw, Warsaw, Poland
(Received 9 September 1977)

The general equation on radiation-induced solid state polymerization given in our previous paper has been applied to the description of the polymerization of a large N-tert-alkylacrylamide series. Due to the similar structure of homologue monomers some mathematical simplifications could be introduced in the equation. The comparison of experimental data with theoretical considerations shows that the relationship describes the process of solid state polymerization of the N-tert-alkylacrylamide series in a satisfactory way for comparatively large limit of conversion.

INTRODUCTION

In comparison with numerous publications describing the solid state polymerization of other crystalline monomers very few papers have been devoted to the process of radiation-induced polymerization in the solid state of N-substituted acrylamides and methacrylamides[1-4] and especially of N-tert-alkylacrylamides[1] with the exception of our own publications[5-14]. As has been pointed out in the former papers[7,8] the main object of these investigations was the study of effect of different factors on the solid state polymerization of the N-substituted alkylacrylamides and the influence of small changes in structure of particular monomers on their reactivity in the solid state in comparison with their reactivity in solution.

EXPERIMENTAL

The methods used for the synthesis of monomers of the N-tert-alkylacrylamide series[8] as well as of the N-arylacrylamide and N-arylmethacrylamide series[2,7,9] has been previously described.

A series of monomers has been synthesized. Special attention was paid to very careful purification necessary to get comparable results.

Irradiations were performed with a ^{60}Co γ-ray source at a temperature of 28°C in an atmosphere of pure nitrogen free of any traces of oxygen.

Separation of unreacted monomer from polymer was carried out by extraction with a methanol—water mixture in a ratio depending on the monomer used. For comparison a titrimetric bromide—bromine method was used also. The polymer after separation was washed and dried to constant weight.

In this manner the radiation-induced solid state polymerization of the monomers mentioned above was investigated in identical experimental conditions.

RESULTS AND DISCUSSION

The list of monomers obtained, their chemical formulae, the time of irradiation, t, and corresponding conversion, S, of particular monomers as well as reduced time $\theta = t_{1/2}^{-1}t$, calculated from experimental data are given in *Table 1*.

Examination of the results shows that in the case of N-tert-alkylacrylamides and N-sec-alkylacrylamides polymerization in the solid state proceeds to almost 100% conversion.

However the polymerization rate is very different for particular monomers but this can be explained by differences in the structure of substituents and the geometrical arrangement of monomer molecules in the crystals.

It is interesting to point out that the increase of substituent does not always imply a decrease of the reactivity in the solid state.

For example, for the series of N-tert-alkylacrylamides with two methyl groups on the tertiary carbon atom and with the increasing third alkyl group the polymerization rate also increases. Conversion *versus* time of irradiation of these monomers is given in *Figure 1*.

Tert-alkylacrylamides having 3 identical groups such as N-tert-butylacrylamide with 3 methyl groups, N-tert-heptylacrylamide with 3 ethyl groups and N-tetradecylacrylamide with 3 butyl groups are characterized by a very low reactivity in the solid state in comparison with other monomers of this series. It is interesting also to observe that isomers with more branched structure are distinguished by a lower reactivity in the solid state.

In comparison with N-tert-alkylacrylamides the solid state polymerization of N-arylacrylamides and especially of N-arylmethacrylamides proceeds very slowly, a fact which is connected with the stabilizing effect of aromatic rings and in the case of the methacrylic series by steric hindrances caused by the presence of two substituents.

But even for the N-arylacrylamide series, low conversion was attained for time of irradiation used in our experiment, so that reduced time θ could not be calculated. Monomers with naphtyl substituents like α-naphtylacrylamide, β-naphtylacrylamide, α-naphtylmethacrylamide and β-naphtylmethacrylamide do not polymerize under the experimental conditions used in our investigations.

Conversion *versus* reduced time for the N-sec- and N-tert-alkylacrylamide series is presented in *Figure 2*.

Taking into account experimental errors it must be admitted that all these points form a chracteristic curve, shown in *Figure 3*.

Table 1 Solid state polymerization of series of *N*-tert-(sec)-alkylacrylamide, *N*-arylacrylamide and *N*-arylmethacrylamide

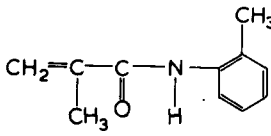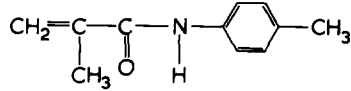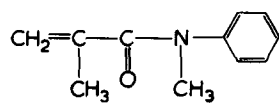| No.	Chemical formula of the monomer	Melting point (°C)	Time of irradiation (h)	Conversion, S (%)	Reduced time
1	$CH_2=CH-C(=O)-NH-C(CH_3)_2-H$	63	4	4.4	0.28
			7	8.3	0.5
			12	29	0.85
			17	81	1.21
			24	99.5	1.7
2	$CH_2=CH-C(=O)-NH-C(CH_3)(H)-C_2H_5$	36	2	5.6	0.377
			4	20.2	0.736
			6	70.5	1.132
			8	97	1.509
			10	99	1.888
3	$CH_2=CH-C(=O)-NH-C(CH_3)_2-CH_3$	128.8	15	3	0.181
			25	4.7	0.303
			40	8	0.483
			60	19.6	0.727
			90	62.8	1.086
			120	96.6	1.448
4	$CH_2=CH-C(=O)-NH-CH(CH_3)-C_3H_7$	29	2	6	0.39
			4	23	0.78
			6	76.2	1.17
			8	98.5	1.57
			10	100	1.95
5	$CH_2=CH-C(=O)-NH-C(CH_3)(H)-CH(CH_3)-CH_3$	70.9	7	4.6	0.31
			17	22.2	0.77
			24	62.8	1.09
			30	94	1.38
			43	100	1.9
6	$CH_2=CH-C(=O)-NH-C(CH_3)(CH_3)-C_2H_5$	92	5	3.2	0.208
			7.5	6	0.313
			20	27	0.834
			23	44	0.958
			24.5	53.8	1.021
			27.5	74.5	1.145
			30	84.5	1.250
7	$CH_2=CH-C(=O)-NH-C(CH_3)(CH_3)-C_3H_7$	64.1	3	3.5	0.30
			4	7.7	0.37
			5	12.6	0.625
			6	19.5	0.730
			7	32	0.875
			10	84	1.250
8	$CH_2=CH-C(=O)-NH-C(CH_3)(C_2H_5)-C_2H_5$	91.8	10	8.2	0.466
			15	18	0.714
			17	27.4	0.809
			24	71.5	1.142
			30	95	1.43
			40	99	1.95
9	$CH_2=CH-C(=O)-NH-C(CH_3)(CH_3)-CH(CH_3)(CH_3)$	100	7	4.7	0.295
			12	9	0.500
			17	19	0.71
			24	49.2	1.00
			30	39.5	1.80
10	$CH_2=CH-C(=O)-NH-CH$ (cyclohexyl)	113	15	3.3	0.167
			40	7.5	0.445
			75	28	0.834
			90	50.5	1.00
			130	98	1.555
11	$CH_2=CH-C(=O)-NH-C(CH_3)(CH_3)-C_4H_9$	61.1	5	6.2	0.40
			7	10.4	0.56
			10	30	0.80
			12	45.6	0.96
			15	80.5	1.20
			17	94	1.36

Table 1 continued

No.	Chemical formula of the monomer	Melting point (°C)	Time of irradiation (h)	Conversion S (%)	Reduced time
12	$CH_2=CH-\underset{\underset{O}{\parallel}}{C}-\underset{H}{N}-\underset{\underset{C_2H_5}{\mid}}{\overset{CH_3}{\underset{\mid}{C}}}-C_3H_7$	79.9	7	5.2	0.35
			12	12	0.60
			17	23.6	0.85
			24	80.5	1.20
			30	98	1.50
13	$CH_2=CH-\underset{\underset{O}{\parallel}}{C}-\underset{H}{N}-\underset{\underset{C_2H_5}{\mid}}{\overset{C_2H_5}{\underset{\mid}{C}}}-C_2H_5$	113.8	17	3.1	0.243
			24	5.6	0.343
			43	15.8	0.643
			75	60	1.07
			92	83.9	1.227
			109	98	1.557
14	$CH_2=CH-\underset{\underset{O}{\parallel}}{C}-\underset{H}{N}-\underset{\underset{C_2H_5}{\mid}}{\overset{CH_3}{\underset{\mid}{C}}}-\overset{CH_3}{\underset{\underset{CH_3}{\mid}}{CH}}$	68	4	4	0.223
			7	6.8	0.388
			17	42.5	0.942
			24	83.2	1.333
			30	99	1.666
15	$CH_2=CH-\underset{\underset{O}{\parallel}}{C}-\underset{H}{N}-\underset{\underset{CH_3}{\mid}}{\overset{CH_3}{\underset{\mid}{C}}}-\overset{CH_3}{\underset{\underset{C_2H_5}{\mid}}{CH}}$	72	7	4.5	0.285
			17	17.5	0.693
			24	48	0.980
			30	84.5	1.224
			45	99.5	1.755
16	$CH_2=CH-\underset{\underset{O}{\parallel}}{C}-\underset{H}{N}-\underset{\underset{CH_3}{\mid}}{\overset{CH_3}{\underset{\mid}{C}}}-CH_2-\overset{CH_3}{\underset{\underset{CH_2}{\mid}}{CH}}$	79	17	4.5	0.354
			30	11.8	0.625
			43	33.6	0.895
			65	94	1.350
17	$CH_2=CH-\underset{\underset{O}{\parallel}}{C}-\underset{H}{N}-\underset{\underset{CH_3}{\mid}}{\overset{CH_3}{\underset{\mid}{C}}}-C_5H_{11}$	30.2	2	7.7	0.476
			4	42	0.95
			5	78	1.18
			6	94.5	1.42
			8	98.8	1.66
18	$CH_2=CH-\underset{\underset{O}{\parallel}}{C}-\underset{H}{N}-\underset{\underset{C_2H_5}{\mid}}{\overset{CH_3}{\underset{\mid}{C}}}-C_4H_9$	42.3	4	4.4	0.3
			7	10	0.55
			12	44.8	0.97
			17	91	1.32
			24	95	1.4
19	$CH_2=CH-\underset{\underset{O}{\parallel}}{C}-\underset{H}{N}-\underset{\underset{C_2H_5}{\mid}}{\overset{C_2H_5}{\underset{\mid}{C}}}-C_3H_7$	63.4	2	3.8	0.20
			4	6.6	0.40
			7	17	0.70
			12	98.5	1.7
20	$CH_2=CH-\underset{\underset{O}{\parallel}}{C}-\underset{H}{N}-\underset{\underset{C_3H_7}{\mid}}{\overset{CH_3}{\underset{\mid}{C}}}-C_3H_7$	85.5	7	5.5	0.38
			12	9.4	0.54
			17	25	0.80
			24	53.6	1.00
			30	93	1.35
21	$CH_2=CH-\underset{\underset{O}{\parallel}}{C}-\underset{H}{N}-\underset{\underset{CH_3}{\mid}}{\overset{CH_3}{\underset{\mid}{C}}}-CH_2-CH_2-\overset{CH_3}{\underset{\underset{CH_3}{\mid}}{CH}}$	34.5	2	5.8	0.384
			4	23	0.769
			6	73.7	1.154
			8	97	1.538
			10	100	1.923
22	$CH_2=CH-\underset{\underset{O}{\parallel}}{C}-\underset{H}{N}-\underset{\underset{CH_3}{\mid}}{\overset{CH_3}{\underset{\mid}{C}}}-CH_2-\underset{\underset{CH_3}{\mid}}{\overset{H}{\underset{\mid}{C}}}-CH_3$	83.2	17	4.6	0.309
			30	9.6	0.545
			43	23.5	0.78
			65	65	1.09
			90	99	1.67
23	$CH_2=CH-\underset{\underset{O}{\parallel}}{C}-\underset{H}{N}-\underset{\underset{C_2H_5}{\mid}}{\overset{CH_3}{\underset{\mid}{C}}}-CH_2-\overset{CH_3}{\underset{\underset{CH_3}{\mid}}{CH}}$	89.1	17	4.2	0.309
			30	9.8	0.545
			43	23.5	0.78
			65	64.8	1.09
			92	99.5	1.67

Table 1 continued

No.	Chemical formula of the monomer	Melting point (°C)	Time of irradiation (h)	Conversion S (%)	Reduced time
24	$CH_2{=}CH{-}C(O){-}NH{-}C(CH_3)_2{-}C_6H_{13}$	29.5	2 4 5 6 8	7 33 65.6 90 99.5	0.44 0.88 1.1 1.3 1.77
25	$CH_2{=}CH{-}C(O){-}NH{-}C(CH_3)(C_3H_7){-}C_4H_9$	52.9	4 7 12 17	4 8.5 30.2 82.3	0.28 0.51 0.857 1.214
26*	$CH_2{=}CH{-}C(O){-}NH{-}C(C_2H_5)_2{-}C_4H_9$	67.5	4 7 17 24 30	3.7 6.2 50.4 81.9 99.8	0.235 0.412 1.010 1.235 1.765
27*	$CH_2{=}CH{-}C(O){-}NH{-}C(CH_3)(C_3H_7){-}CH_2{-}CH(CH_3)_2$	80.2	17 30 43 65	3.6 11.3 23 86.3	0.327 0.578 0.765 1.250
28*	$CH_2{=}CH{-}C(O){-}NH{-}C(CH_3)(C_4H_9){-}CH_2{-}CH(CH_3)_2$	79.9	17 30 43 65	4.7 10.6 28.4 92.5	0.320 0.587 0.843 1.34
29*	$CH_2{=}CH{-}C(O){-}NH{-}C(C_2H_5)(C_4H_9){-}C_4H_9$	45	7 12 17 24 30	3.4 9.6 22.6 64.1 91.5	0.218 0.54 0.77 1.08 1.32
30*	$CH_2{=}CH{-}C(O){-}NH{-}C(C_3H_7)(C_4H_9){-}C_4H_9$	63.1	7 17 3? 4? 60	3.2 8.2 38.8 90 99	0.212 0.512 0.909 1.303 1.81
31*	$CH_2{=}CH{-}C(O){-}NH{-}C(C_4H_9)_2{-}C_4H_9$	99.8	17 30 43 65 90	5 13.7 33.9 92 99	0.35 0.638 0.890 1.354 1.87
32	$CH_2{=}CH{-}C(O){-}NH{-}C_6H_5$	105.5	24 72 120 192	1.6 4.32 7.31 9.81	
33	$CH_2{=}CH{-}C(O){-}NH{-}C_6H_4(2{-}CH_3)$	110	24 72 120 192	0.85 3.22 4.41 5.8	
34	$CH_2{=}CH{-}C(O){-}NH{-}C_6H_4{-}CH_3$	143.5	24 72 120 192	1.4 3.75 6.21 9.45	
35	$CH_2{=}CH{-}C(O){-}N(CH_3){-}C_6H_5$	76.5	24 72 120 192	1.2 2.81 9.64 16.8	
36	$CH_2{=}C(CH_3){-}C(O){-}NH{-}C_6H_5$	86.5	24 72 120 192	1.24 2.60 3.54 3.88	

Table 1 continued

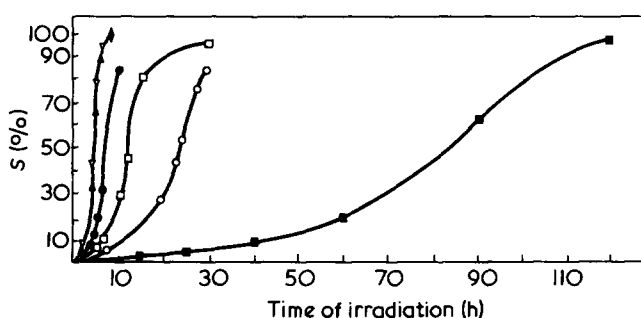| No.	Chemical formula of the monomer	Melting point (°C)	Time of irradiation (h)	Conversion S (%)	Reduced time
37		95.5	24	1.46	
			72	3.74	
			120	5.28	
			192	5.41	
38		89.3	24	2.5	
			72	5.64	
			120	7.24	
			192	7.59	
39		61.5	24		
			72	1.46	
			120	1.82	
			192	1.97	

*   Obtained for the first time in our laboratory

Figure 1 Solid state polymerization of homologous series of N-tert-alkylacrylamides with two methyl groups increasing alkyl group on the tertiary carbon atom. ■, N-tert-butylacrylamide; ○, N-tert-amylacrylamide; ●, N-tert-hexylacrylamide/N-1,1-dimethylbutylacrylamide; □, N-tert-heptylacrylamide/N-1,1-dimethylamylacrylamide; ▽, N-tert-octylacrylamide/N-1,1-dimethylhexylacrylamide and ▲, N-tert-nonylacrylamide/N-1,1-dimethylheptylacrylamide
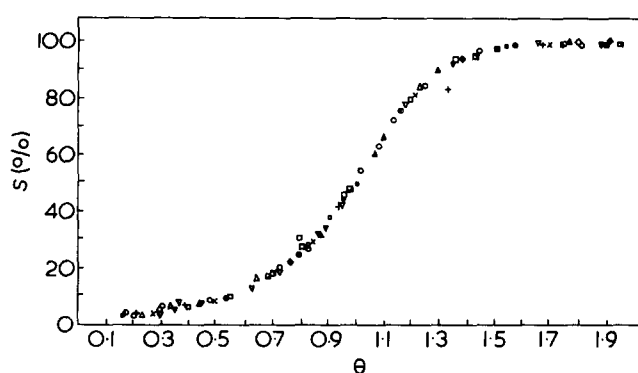

Figure 2 Radiation-induced solid state polymerization of an homologous series of N-tert-(N-sec)-alkylacrylamides. S, conversion; θ, reduced time

APPLICATION OF THE THEORETICAL EQUATION TO THE DESCRIPTION OF SOLID STATE POLYMERIZATION OF N-TERT-ALKYLACRYLAMIDE SERIES

Starting from the equation derived in a preceeding paper (part 1)

$$-\frac{\beta M_0}{M(M_0 - M)}\left(\frac{\beta M_0 + \gamma M}{M_0 - M}\right)^{n_0-1} dM$$

$$= K_p m^{-n_0}\left\{1 + \left[\frac{1}{2}g''(t)_{t=0}\ln(m \cdot d_{pol}) - \frac{n_0}{m}\bar{M}_p''(t)_{t=0}\right]t^2\right\}dt \quad (1)$$

and assuming in the simplest case that $n_0 = 1$ the following relationship is obtained:

$$-\frac{\beta M_0}{M(M_0 - M)}dM = K_p m^{-1}\left\{1 + \frac{1}{2}\left[g''(t)_{t=0}\ln(m \cdot d_{pol}) - \frac{1}{m}\bar{M}_p''(t)_{t=0}\right]t^2\right\}dt$$

substituting conversion S for M by:

$$S = \frac{M_0 - M}{M_0}$$

the equation becomes after integrating:

$$\log\frac{S}{1-S} = K_p m^{-1}\left\{t + \frac{1}{6}\left[g''(t)_{t=0}\ln(m \cdot d_{pol}) - \frac{1}{m}\bar{M}_p''(t)_{t=0}\right]t^3\right\} + \text{constant}$$

Introducing the reduced time

$$\theta = t_{1/2}^{-1}t$$

gives

$$\log\frac{S}{1-S}$$

$$= K_p(\beta m)^{-1}t_{1/2}\left\{\theta + \frac{1}{6}\left[g''(t)_{t=0}\ln(m \cdot d_{pol}) - \frac{1}{m}\bar{M}_p''(t)_{t=0}t_{1/2}^2\right]\theta^3\right\} + \text{constant}$$
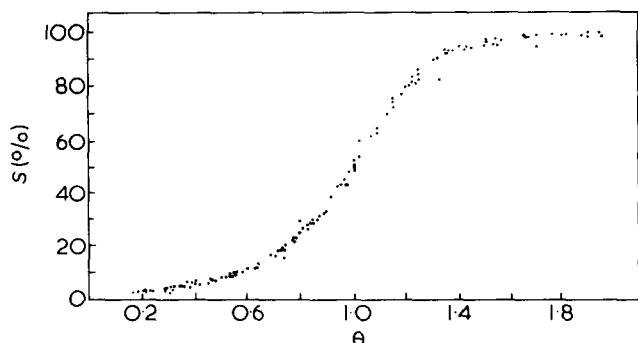
Figure 3 Conversion as a function of reduced time, θ, for an homologous series of N-tert-(N-sec)-alkylacrylamides

$$\text{constant} = -\left[K_p(\beta_m)^{-1}t_{1/2}\right]\left\{1 + \frac{1}{6}\left[g''(t)_{t=0}\ln(m \cdot d_{\text{pol}}) - \frac{1}{m}\bar{M}_p''(t)_{t=0}\right]t_{1/2}^2\right\}$$

and after rearrangement

$$\ln\frac{S}{1-S}$$

$$= K_p(\beta_m)^{-1}t_{1/2}\left\{(\theta-1) + \frac{1}{6}\left[g''(t)_{t=0}\ln(m \cdot d_{\text{pol}}) - \frac{1}{m}\bar{M}_p''(t)_{t=0}\right]t_{1/2}^2(\theta^3-1)\right\} \quad (2)$$

Denoting, for the 'i' homologue monomers:

$$K_{pi}(\beta_i m_i)^{-1}t_{i,1/2} \equiv A_{0i}$$

and

$$\frac{1}{6}\left[g_i''(t)_{t=0}\log(m_i d_{i,\text{pol}}) - \frac{1}{m_i}\bar{M}_{ip}''(t)_{t=0}\right]t_{i,1/2}^2 \equiv B_{0i}$$

Equation (2) for each monomer of the series can be presented in the following form:

$$\ln\frac{S}{1-S} = A_{0i}[(\theta-1) + B_{0i}(\theta^3-1)] \quad (3)$$

In the case when for the whole series of homologue monomers all: $A_{0i} = id \equiv A_0$ and $B_{0i} \equiv id \equiv B_0$ then the equation:

$$\ln\frac{S}{1-S} = A_0[(\theta-1) + B_0(\theta^3-1)] \quad (4)$$

would have a general character describing the 'universal curve' for all the series mentioned above.

In the case when the identity A_0 and B_0 would not occur for the given series of homologues monomers, in the place of one curve *versus* θ a whole family of curves will be obtained intersecting at $S = 0.5$ $\theta = 1$.

Taking into account mathematical simplifications introduced during the derivation of the final relationship between degree of conversion and time of polymerization, no theoretical consequences could be deduced from the fact of the identity of A_0 and B_0 of all the series of monomers studied above.

COMPARISON OF EXPERIMENTAL DATA WITH THEORETICAL CONSIDERATIONS

From the equation (4) the following relationship can be derived:

$$P(S) + cG(\theta) = 0 \quad (5)$$

where

$$P(S) \equiv \ln\frac{S}{1-S} \quad (6)$$

$$G(\theta) \equiv (\theta-1) + B_0(\theta^3-1) \quad (7)$$

Substituting the experimental data of conversion obtained for the solid state radiation polymerization of the series of monomers mentioned above (*Table 1*) corresponding values of $\log S/(1-S)$ are calculated.

Extrapolation of $\log S/(1-S)$ *versus* θ to the value $\theta = 0$ enables us to obtain a relation between A_0 and B_0. Using

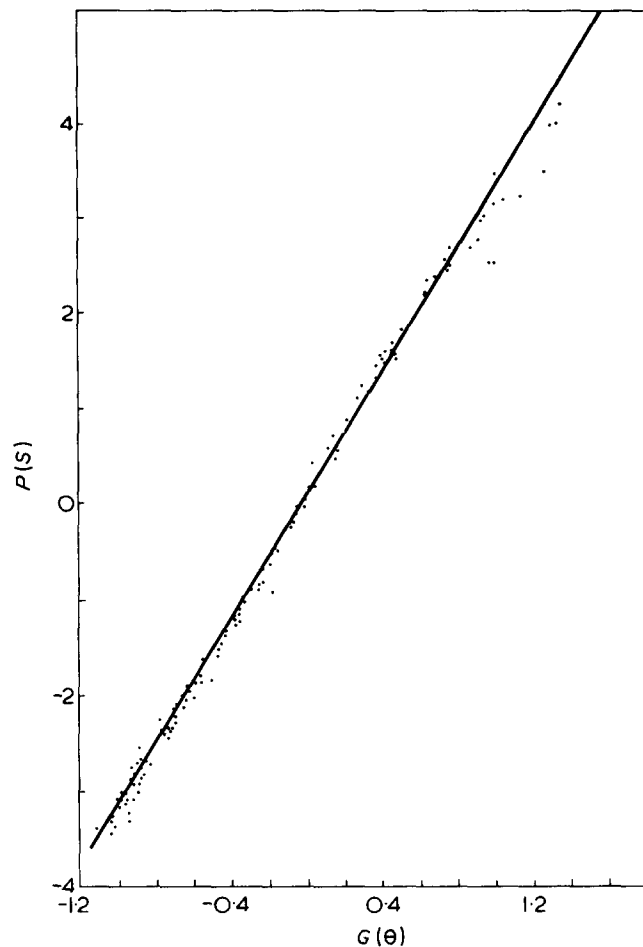*Figure 4* Relation between $P(S) = \ln S/(1-S)$ and $G(\theta) = (\theta-1) + 0.28(\theta^3-1)$

experimental data summarized in *Table 1*, values of the constants A_0 and B_0 are calculated by least square root method. The values obtained are $A_0 = 3.2803$ and $B_0 = 0.28$; $G(\theta)$ is calculated from equation (7).

Substituting the experimental data of conversion S into equation (6) and the corresponding data of reduced time θ from *Table 1* into equation (7) a series of points are obtained in *Figure 4*. $P(S)$ versus $G(\theta)$ distributed more or less symmetrically on both sides of the straight line describing the relation:

$$\ln \frac{S}{1 - S} = 3.2803\,[(\theta - 1) + 0.28(\theta^3 - 1)]$$

Taking into account all the simplifying assumptions made in these considerations and mathematical transformations of the equations as well as some experimental errors it must be admitted that the relationship describes the process of solid state polymerization in a satisfactory way for a comparatively large limit of conversion from 3 to 97% change.

REFERENCES

1 Adler, G. *J. Chem. Phys.* 1959, **21**, 848
2 Jäger, P. and Waight, E. S. *J. Polym. Sci.* 1963, **6**, 1909
3 Kargin, V. A. and Kabanov, V. A. *Zh. Vses. Khim. Ova.* 1964, **9**, 602
4 Azori, H. M., Platé, A. and Kargin, V. A. *Proc. 2nd Symp. Radiation Chem. Tihany*, 1967
5 Zurakowska-Orszàgh, J. 'Solid State polymerization of acrylamide, methacrylamide and *N*-tert amylacrylamide.'
6 Zurakowska-Orszàgh, J. *Congrès de Chimie Industrielle, Varsovie*, 1963
7 Zurakowska-Orszàgh, J. *Chim. Ind.* 1965, **93**, 404
8 Zurakowska-Orszàgh, J. *IUPAC Int. Symp. Macromol. Chem. Prague* 1965
9 Zurakowska-Orszàgh, J. *J. Polym. Sci. (C)* 1968, **16**, 3291
10 Orszàgh, A. and Zurakowska-Orszàgh, J. *Proc. 2nd Symp. Radiation Chem. Tihany*, 1967
11 Zurakowska-Orszàgh, J. and Wojno, T. *J. Polym. Sci. (C)* 1968, **16**, 4219
12 Zurakowska-Orszàgh, J. *IUPAC Symp. Macromol. Chem., Japan*, 1966
13 Swiderski, J. and Zurakowska-Orszàgh, J. *Rocz. Chem.* 1968, **42**, 1299
14 Swiderski, J., Zurakowska-Orszàgh, J. *Rocz. Chem.* 1968, **42**, 1691