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# BRIEF COMMUNICATIONS

## Crystal Structure Transformation in Potassium Acrylate

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Potassium acrylate undergoes a reversible phase transformation around 335°K with an activation energy of 133 kcal/mole. Differential scanning calorimetry and high temperature X-ray powder diffraction techniques have been used to probe this phenomenon.

### Introduction

Gamma radiation induced solid state polymerization reactions of vinyl monomers have been the subject of several investigators (*1–7*). Morawetz and Rubin have studied similar polymerization reactions with alkali acrylates and methacrylates (*2*). Their results are similar to those of other workers including the data on activation energy for the propagation reaction. However, a closer analysis of their activation energy plot for potassium acrylate (p. 671) reveals that the value at 333.3°K departs significantly from the main plot data curve (beyond experimental error). In fact the authors themselves have pointed out this anomaly. It is therefore appropriate to understand why the polymerization reaction at this temperature is different from that at other temperatures. One possible reason could be that the monomer, potassium acrylate, undergoes a crystal phase transition close to the temperature of the reaction. In solid state reactions involving solids which undergo phase transitions it is very well known that the reaction rates undergo a drastic change at the phase transition temperature (*8, 9*). The crystal structure of potassium acrylate at room temperature is orthorhombic (*10*) with space group $P_{2_12_12_1}$. The objective of the present work is to check for a possible phase transition in potassium acrylate near 333°K.

### Experimental

Freshly distilled acrylic acid was slowly added to a cooled solution of potassium hydroxide in methanol to the phenolphthalein endpoint. A slight excess of acid was added and the salt was precipitated by acetone and filtered. The salt was then purified by recrystallization from saturated methanolic solution by acetone vapors in a closed container.

Phase transformation studies were carried out using Du Pont 990 differential scanning calorimeter at heating and cooling rates of 2°C/min. The DSC instrument was calibrated with standard samples such as benzoic acid, naphthalene, and indium for



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temperature and enthalpy output. The fraction of material transformed at a particular temperature was calculated by finding the ratio of the area of the portion of the DSC thermogram at that temperature relative to the total area of the peak.

The peak temperature $T_p$, the departure temperature $T_d$, and the intersection temperature $T_i$ were determined for the phase transformation as described elsewhere (*11*, *14*).

Wide angle X-ray diffraction (WAXD) scans were obtained with a Philips PW 1050/70 vertical goniometer employing a high temperature attachment.

## Results and Discussion

Potassium acrylate undergoes an endothermic change near 337°K during heating at 2°C/min heating rate (Fig. 1a). This endotherm is due to a crystal phase transformation as (i) the sample does not undergo any weight loss as shown by Stanton Redcroft thermogravimetry measurement, (ii) the sample does not melt as is evident from the visual observation using hot stage microscopy at the temperature of interest. In fact the thermal event at 337°K observed in the DSC scan of potassium acrylate is reversible. The sample further undergoes an exothermic change during the cooling scan at the cooling rate of 2°C/min from 363°K (Fig. 1b).

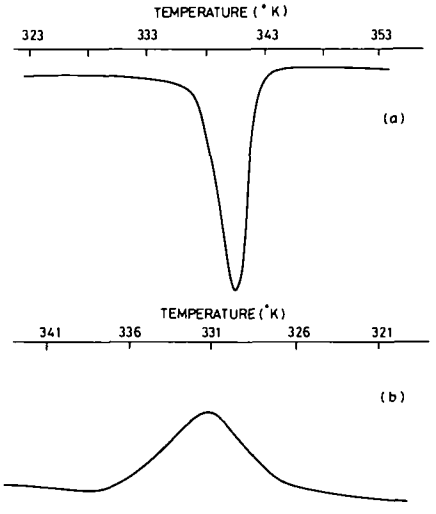


FIG. 1. DSC traces of potassium acrylate. Heating/cooling rate: 2°C/min.

TABLE I

X-RAY DIFFRACTION DATA ON POTASSIUM ACRYLATE

| Temperature 298°K | | Temperature 298°K | |
|---|---|---|---|
| $2\theta$ (deg) | $d$ (Å) | $2\theta$ (deg) | $d$ (Å) |
| 22.9 | 3.88 | 22.1 | 4.02 |
| 25.2 | 3.53 | 23.0 | 3.86 |
| 26.1 | 3.41 | 23.6 | 3.77 |
| 27.5 | 3.24 | 26.1 | 3.41 |
| 28.4 | 3.14 | 26.4 | 3.38 |
| 30.0 | 2.98 | 27.2 | 3.28 |
| 32.4 | 2.76 | 28.35 | 3.15 |
| 33.9 | 2.64 | 31.6 | 2.83 |
| 36.8 | 2.44 | 35.3 | 2.54 |
| 39.6 | 2.28 | 36.8 | 2.44 |
| 40.7 | 2.22 | 39.0 | 2.31 |
| 42.4 | 2.13 | 39.8 | 2.26 |
| 44.3 | 2.04 | 42.0 | 2.15 |
| 45.4 | 2.00 | 45.4 | 2.00 |
| 46.2 | 1.97 | 46.0 | 1.97 |
| 46.8 | 1.94 | 49.9 | 1.83 |
| 49.9 | 1.83 | | |

In order to ascertain whether structural change occurs or not during the transformation, WAXD scans (Cu$K\alpha$) were recorded for a potassium acrylate sample at room temperature (298°K) and at 358°K (Table I). From the fact that the X-ray diffraction patterns taken at room temperature and at 358°K are different, it is evident from Table I that potassium acrylate undergoes a phase transformation.

A closer look at Figs. 1a and b shows that there is considerable hysteresis during the phase transformation due to the strain involved in the reversible phase transformation, as in sulfates and perchlorates, and similar materials (*11–14*). This is further ev-

TABLE II

DSC DATA ON PHASE TRANSFORMATION OF POTASSIUM ACRYLATE

| °K | | | | | | kcal/mole | | | |
|---|---|---|---|---|---|---|---|---|---|
| $T_d^f$ | $T_i^f$ | $T_p^f$ | $T_d^r$ | $T_i^r$ | $T_p^r$ | $\Delta H^f$ | $\Delta H^r$ | $E_a$ | $E_s$ |
| 326 | 337.25 | 339.75 | 338.5 | 337.25 | 331 | 0.54 | 0.58 | 133.3 | 406.2 |

ident from the hysteresis loop constructed (*11*) (Fig. 2) from DSC peaks from the fraction of material transformed at different temperatures in the forward and reverse directions.

From the DSC curves the peak temperature $T_p$, the departure temperature $T_d$, and the intersection temperature $T_i$ were determined for both the forward (Fig. 1a) and reverse (Fig. 1b) transformations the values are summarized in Table II. The energy of activation, $E_a$, was calculated by the method of Piloyan (*15*) to be 133.0 kcal/mole (Table II), with an uncertainty of ±15%. The strain energy for the phase change has been calculated by the method suggested by Rao and Rao (*11*) and it was found to be 406.2 kcal/mole (Table II), which is in reasonable agreement with that obtained for salts such as sulfates and perchlorates, and the like (*11*, *14*). From the areas of the endothermic and exothermic peaks, the enthalpy change for the forward and reverse transformations has been calculated and is presented in Table II.

Thus, the data of the present investigation show that potassium acrylate undergoes a reversible phase transition with an activation energy of 133 kcal/mole.

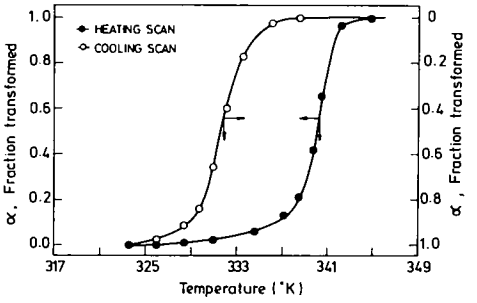


FIG. 2. Hysteresis loop for potassium acrylate phase transformation.

## References


1. B. M. BAYSAL, H. N. ERTEN, AND U. S. RAMELOW, *J. Polym. Sci. Part A-1* **9**, 581 (1971).
2. H. MORAWETZ AND I. D. RUBIN, *J. Polym. Sci.* **57**, 669 (1962).
3. B. M. BAYSAL, G. ADLER, D. BALLANTINE, AND P. COLOMBO, *J. Polym. Sci.* **44**, 117 (1960).
4. B. M. BAYSAL, E. ERGOZ, AND G. ADLER, *J. Pure Appl. Sci.* **12**(1), 1 (1979).
5. K. HAYAKAWA, K. KAWASE, AND H. YAMAKITA, *J. Polym. Sci. Polym. Chem. Ed.* **16**(12), 3307 (1978).
6. J. H. O'DONNELL AND R. D. SOTHMAN, *J. Macromol. Sci. Chem. A* **14**(6), 879 (1980).
7. J. H. O'DONNELL, AND R. D. SOTHMAN, *Radiat. Phys. Chem.* **13**(3–4), 77 (1979).
8. L. L. BIRCUMSHAW AND B. H. NEWMAN, *Proc. R. Soc. Ser. A* **227**, 115 (1954); **227**, 228 (1955).
9. J. N. MAYCOCK AND V. R. PAI VERNEKER, *Proc. R. Soc. Ser. A* **307**, 303 (1968).
10. Powder Diffraction File, JCPOS, 11–934 (1972).
11. C. N. R. RAO AND K. J. RAO, *J. Mater. Sci.* **1**, 238 (1966).
12. H. MAURAS, *C.R. Acad. Sci. Ser. C* **272**, 973 (1971).
13. S. R. YOGANARASIMHAN AND S. K. SYAL, *Inorg. Nucl. Chem. Lett.* **9**, 1193 (1973).
14. V. R. PAI VERNEKER AND K. RAJESHWAR, *Thermochim. Acta* **13**, 305 (1975).
15. G. O. PILOYAN, *Nature (London)* **212**, 1229 (1966).