

CHROMSYMP. 840

DETERMINATION OF CONSTANTLY FORMED VOLATILE REACTION PRODUCT MICROIMPURITIES IN POLYMERIZATION SYSTEMS BY HEADSPACE GAS CHROMATOGRAPHIC ANALYSIS

R. N. MOKEYEVA*, Y. A. TSARFIN and W. ERNST

Analytical Laboratory, All-Union Research Institute for Synthetic Resins, Vladimir (U.S.S.R.)

SUMMARY

To determine acetone microimpurities ($\geq 0.5 \cdot 10^{-5}\%$) formed during polyoxypropylene polyol (POP) synthesis, a method has been proposed that involves continuous gas extraction and subsequent GC of the equilibrium vapour phase.

The influence of temperature and duration of gas extraction, acetone and propylene oxide concentrations and molecular weight of POP on the partition coefficient for the alkaline POP-argon system have been studied. The effect of the gas extraction rate and duration on the specific rate of acetone formation was investigated, and the activation energy of acetone formation reactions was determined.

The proposed method is applicable to the determination of continuously formed microimpurities in volatile compounds of polymerization systems.

INTRODUCTION

Previously we described the determination of volatile microimpurities in alkaline polymerizates by continuous gas extraction and headspace gas chromatography (GC)^{1,2}. This method is applicable only to stable polymerization systems with a constant content of volatile substances.

Whilst studying alkaline polyoxypropylene polyol (POP) by continuous gas extraction, it was noted that the content of microimpurities of C₁-C₇ hydrocarbon, ethylene and propylene oxides, acetaldehyde, propionaldehyde and isopropanol, as expected, decreased and asymptotically approached zero, whereas the acetone content decreased to a constant value governed by the gas flow-rate and temperature. The above phenomenon is possible if in a system acetone is formed and in the process of gas extraction equilibrium is achieved between the acetone formed and extracted in unit time. In the presence of an alkaline catalyst, propylene oxide polymerization is accompanied by depolymerization of POP at the chain ends with the formation of acetone, which is the source of some impurities that accumulate in the polymerizate.

In this paper, a method is described that is applicable to the determination of volatile microimpurities whose concentration is constantly increasing in polymerization systems.

EXPERIMENTAL

Headspace GC and calibration with acetone were carried out with Tsvet-5 chromatograph, a flame ionization detector and a 3×0.03 m I.D. glass column packed with 20% polyethylene glycol succinate on Chromosorb W (60–80 mesh) at 80°C and a carrier gas (argon) flow-rate of 38 ml/min.

The apparatus was calibrated with standard solutions of acetone in dichloroethane or propanol within the concentration range 0.25–0.50%, the volume of solution injected into the evaporator being 1–2 ml.

The amount of compound per cm^2 of area peak (T g/ cm^2) or per cm of peak height (T , g/cm) of acetone was calculated from the equation

$$T \text{ (g/cm}^2 \text{ or g/cm)} = \frac{V_1 dc}{100 A} \quad (1)$$

where V_1 = volume (ml) of standard acetone solution injected, d = specific gravity of solvent (g/ml), c = mass fraction of acetone (%) in standard solution and A = peak area or height (cm^2 or cm).

An equilibrium vapour phase was injected using a six-way gas distribution tap with a 1-mm loop. The injector was maintained at 120°C in a thermostat for chromatograph detectors.

Acetone gas extraction was carried out in a 20-ml water-jacketed gas extraction vessel with a glass filter, which was supported over the thermostat containing the injector unit. The vessel was closed with a silicone-rubber plug and was connected to the injector with a stainless-steel welded needle-point capillary. Samples were thermostated with an accuracy of $\pm 0.02^\circ\text{C}$ using a thermostat. Alkaline POPs with a viscosity range from 100 to 1000 mPa · s and molecular weights of 300–5000 were studied.

The method for the determination of acetone microimpurities in alkaline polymerizates of propylene oxide was as follows.

About 4 g of alkaline POP were placed in the vessel for gas extraction, which was closed with a silicone-rubber plug and connected to the previously heated (50 – 90°C) water thermostat. It was then connected to the injector with the stainless-steel needle-point capillary. Argon for gas extraction was injected at a rate of 15–60 ml/min. Sampling for chromatographic analysis was performed 5 min after gas extraction had begun and was stopped after a constant acetone peak area ($S_{\text{const.}}$) on the gas extract chromatogram was achieved (see Fig. 1).

The acetone peak area was calculated from the chromatogram obtained, and the calculation of the acetone peak area that corresponds to an acetone concentration in the gas phase of C_g^0 at $\tau = 0$ was carried out by extrapolating the curve $\ln(S_i - S_{\text{const.}}) = f(\tau)$ to the ordinate, where S_i = acetone peak area at the i th sampling of gas extracted (cm^2), $S_{\text{const.}}$ = equilibrium acetone peak area at a given rate and temperature and τ = time (min) of gas extraction (see Fig. 2).

The acetone concentration in the polymerizate studied at the beginning of gas extraction (C_1^0) was calculated from the following equation, which we derived previously^{1,2}:

$$C_1^0 = \frac{C_g^0 \bar{v}}{\beta V_1} = \frac{S^0 T \bar{v}}{\beta V_1} \quad (2)$$

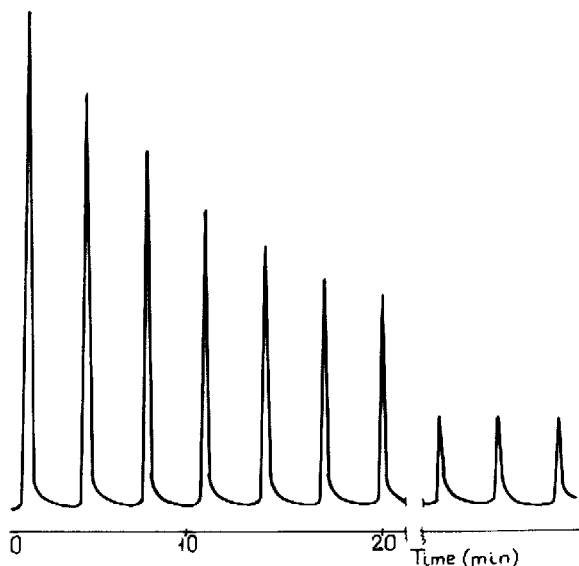


Fig. 1. Acetone concentration changes in the equilibrium gas phase during extraction.

where β is the slope of the curve $\ln(S_i - S_{\text{const.}}) = f(\tau)$ (min^{-1}), \bar{v} is the gas flow-rate (ml/min) and V_1 is the volume of the polymerizate studied (ml).

RESULTS AND DISCUSSION

Table I gives the results for acetone concentrations determined alkaline POP. The reproducibility of the determination of acetone by continuous gas extrac-

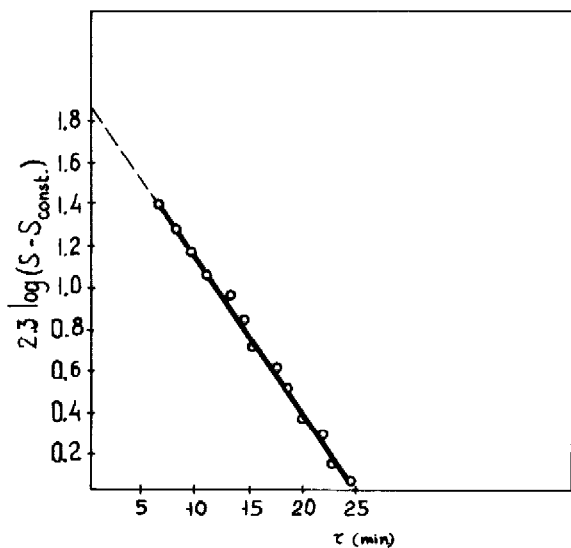


Fig. 2. Graph of the relationship $\ln(S_i - S_{\text{const.}}) = f(\tau)$. $\bar{v} = 17.0 \text{ ml}/\text{min}$; $V_1 = 4.27 \text{ ml}$.

tion at a concentration in a sample of $0.78 \cdot 10^{-5}\%$ is characterized by a relative mean square error (S_r) of 1.8%.

In eqn. 2 for the calculation of the contents of a volatile compound in the reaction system, the ratio $\tilde{v}/\beta V_1$ is the partition coefficient (K) of the compound studied in the POP-argon system. The determination of the partition coefficient for the acetone formed in the reaction of depolymerization of POP at the chain ends is very important for the optimal choice of propylene oxide polymerization conditions and the separation of by-products from the polymerizate.

The partition coefficient was either calculated from

$$K = \frac{\tilde{v}}{\beta V_1} \quad (3)$$

where β was graphically defined as the slope of the curve $\ln(S_i - S_c) = f(\tau)$ or from the equation

$$K = \frac{(\tau_n - \tau_1)\tilde{v}}{2.3 \log \frac{(S_1 - S_{\text{const.}})}{(S_n - S_{\text{const.}})} - V_1} \quad (4)$$

where τ_1 and τ_n are the times of the first and the n th sampling of the gas extract (min), S_1 and S_n are the acetone peak areas for the first and the n th sampling (cm^2) and $S_{\text{const.}}$ is the equilibrium value of the acetone peak area. The relative square mean error for the partition coefficient of acetone in the POP-argon systems at $K = 79.9\%$ ($n = 10$, $\alpha = 0.95$) is 2.1%.

The influence of different factors on the partition coefficient of the alkaline POP-argon system is shown in Table II.

It was concluded from the results that K is constant with time, acetone concentration in the polymer and molecular weight (OH group content) in the ranges studied. However, it is strongly influenced by the propylene oxide content in the polymerizate.

TABLE I
ACETONE CONCENTRATIONS IN POP

Sample No.	Concentration (%)				
	Total alkalinity	Salt alkalinity	OH value	Propylene oxide	Acetone ($\text{g/ml} \cdot 10^{-5}$)
1	2.17	0.07	8.3	11.23	0.51
2	1.98	0.11	6.2	7.25	0.32
3	0.87	0.08	3.9	6.88	1.88
4	0.72	0.10	2.5	5.05	0.85
5	0.51	0.05	1.8	5.48	0.75
6	0.42	0.05	1.4	3.33	1.24
7	0.36	0.07	1.3	2.88	0.98
8	0.34	0.06	1.2	3.48	0.77

TABLE II
EFFECT OF EXTRACTION CONDITIONS AND POLYMERIZATE PROPERTIES ON *K*

Gas extraction flow-rate, 16.5 ml/min.

<i>Sample 1</i> (50°C)		<i>Sample 2</i>		<i>Sample 3</i> (50°C)		<i>Sample 4</i> (50°C)		<i>Sample 5</i> (100°C)	
τ (min)	<i>K</i>	Temperature (°C)	<i>K</i>	Acetone concentration (g/ml · 10 ⁻⁵)	<i>K</i>	Propylene oxide concentration (%)	<i>K</i>	OH value	<i>K</i>
11	87.15	40	103.50	16.7	80.1	0	80.5	2.51	31.6
21	89.13	50	80.17	17.6	78.2	2.9	103.1		
29	86.85	60	70.81	35.8	77.7	3.5	115.1	3.86	31.07
46	89.51	70	61.26	45.5	83.9	5.1	130.1		
56	89.01	80	50.80	46.2	82.9	6.9	155.5	6.53	31.74
66	88.72	90	42.05	50.1	79.2	11.2	253.4		
74	89.24	100	30.63	51.6	76.1	—	—		

It should be noted that the proposed acetone gas extraction could be carried out in the gas flow-rate range 15–60 ml/min provided that the thermodynamic equilibrium in the POP–argon system was maintained and the amounts of acetone formed and extracted in unit time were balanced. This is confirmed by the fact that $C_{\text{const.}}\bar{v}$ is constant for gas flow-rates within the range of equilibrium saturation of the gas flow with acetone vapour. The relationship

$$V_{\text{Spec.}} (\text{min}^{-1}) = \frac{C_{\text{const.}}\bar{v}}{q} \quad (5)$$

where q is the sample weight (g), gives the specific rate of acetone formation in alkaline POP. $V_{\text{Spec.}}$ is constant and is not influenced by the gas flow-rate or duration of extraction.

Values of the specific rate of acetone formation (see Table III) indicate that thermodynamic equilibrium was established in the system. The relative mean square error for the determination of $V_{\text{Spec.}}$ at $n = 40$ and $\alpha = 0.95$ is 1.6%.

The specific rate of compound formation, as indicated by the experimental data, is constant at a given temperature for the system studied and is influenced only by the nature of the components present.

Based on the influence of temperature on the specific rate of acetone formation, the activation energy for the reaction of acetone formation was determined. Taking the logarithm of the equation of the compound formation reaction:

$$K = K_0 e^{-E_A/RT} \quad (6)$$

we obtain

$$\ln K = \ln K_0 - \frac{E_A}{RT} \quad (7)$$

where E_A is the activation energy of the compound formation (kcal/K · mol), K and K_0 are constants of the rate of the compound formation at temperatures T and T_0 , respectively, and $R = 1.958$ cal/K · mol.

TABLE III

INFLUENCE OF GAS FLOW-RATE (\bar{v}) AND TIME (τ) ON THE SPECIFIC RATE OF ACETONE FORMATION AT 80°C

\bar{v} (ml/min)	$V_{\text{Spec.}} \cdot 10^{-7}$ (min ⁻¹)	τ (min)	$V_{\text{Spec.}} \cdot 10^{-7}$ (min ⁻¹)
14.5	2.09	90	2.06
15.8	2.02	120	1.99
17.9	2.03	180	2.02
19.8	2.12	240	2.02
22.4	2.08	300	2.01
24.8	2.07	410	2.05

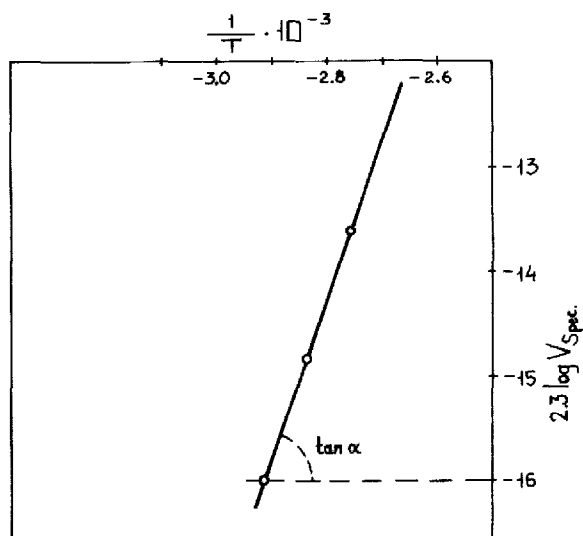


Fig. 3. Graph of the relationship $\ln V_{Spec.} = f(T^{-1})$ for POP 300.

TABLE IV

ACTIVATION ENERGY FOR THE REACTION OF ACETONE FORMATION AT 80°C FOR POP 300 POLYMERIZATE

Total alkalinity, Σ (%)	Salt alkalinity, Σ (%)	E_d (kcal/K · mol)
4.46	0.06	32.208
0.92	0.03	35.541
1.71	0.07	29.385

Eqn. 6 is linear with a slope equal to

$$\tan \alpha = \frac{E_d}{R} \quad (8)$$

from which

$$E_d = R \tan \alpha \quad (9)$$

By plotting the logarithmic relationship of the acetone formation rate, $\ln V_{Spec.} = \ln K = f(T^{-1})$, it is possible to find the activation energy of acetone formation from eqn. 9 (see Fig. 3).

Table IV gives the results for the determination of the activation energy for the reaction of acetone formation in alkaline propylene oxide polymerizates.

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