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Thermogravimetric Analysis of Vinylacetate-Vinylbutyrate Copolymers

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SUMMARY:

The composition of copolymers of vinylacetate (VAc) and vinylbutyrate (VB) can be determined rapidly and satisfactorily by dynamic thermogravimetric analysis (TGA), in spite of the fact that both acetic and butyric acid are abstracted simultaneously and incompletely from their respective segments. The TGA results are compared with those obtained by gaschromatographic analysis of the reaction mixtures during copolymerization, and are within experimental error. Extension of this analysis method to other binary vinylester combinations seems to be possible.

ZUSAMMENFASSUNG:

Die Zusammensetzung von Copolymeren aus Vinylacetat (VAc) und Vinylbutyrat (VB) kann schnell und mit genügender Genauigkeit mittels dynamischer thermogravimetrischer Analyse (TGA) festgestellt werden, obgleich Essigsäure und Buttersäure zu gleicher Zeit und unvollständig aus den diesbezüglichen Segmenten abgespalten werden. Die TGA-Resultate werden mit aus gaschromatographischen Analysen erzielten Ergebnissen verglichen; sie liegen innerhalb der experimentellen Fehler. Die Ausweitung auf andere binäre Vinylester-Kombinationen ist wahrscheinlich möglich.

Introduction

Although determination of copolymer composition is no longer a necessity for calculating reactivity ratios^{1,2}, it is imperative on describing and controlling copolymer properties, and the search for new, more accurate and especially more rapid methods for copolymer analysis still continues. Recent reports^{3,4} on compositional analysis of vinylacetate-vinylpropionate copolymers are the outcome of above efforts. Aydin et al.³ applied combined gaschromatographic and potentiometric techniques for estimating the aliphatic acids liberated in a melt containing copolymer and p-toluenesulfonic acid, and Hirai⁴ resorted

to IR and NMR spectroscopy as analytical tools. The tracer technique used by Bevington et al.⁵ for the quantitative analysis of some vinylacetate-vinylester copolymers is a general method, in principle applicable to all copolymers. In practice, however, difficulties arise since it requires laborious synthetic techniques involving labelled monomers.

The application of thermogravimetric analysis (TGA) in this field was limited to copolymers either having different decomposition temperatures for both monomer sequences, or having only one decomposable monomer. Thus, TGA has been used satisfactorily^{6,7} for the compositional analysis of ethylene-VAc copolymers. The primary decomposition of PVAc⁸ as well as of its copolymers has been attributed to the practically quantitative abstraction of acetic acid at 300–380°C. Gilbert et al.⁹ reported the abstraction of butyric acid from polyvinylbutyrate (PVB) within about the same temperature interval.

The present investigation shows that compositional analysis of VAc-VB copolymers can be carried out successfully by dynamic TGA in spite of the fact that only one decomposition temperature range is registered in this case.

Experimental

Materials

Vinylacetate

Technically pure VAc (Konam) was purified by distillation in a column (height 1.60 m, diameter 36 mm) packed with glass Fenske helices (diameter 3 mm). The fraction having b.p. 72–73°C and refractive index $n_D^{20} = 1.3955$ was collected and used.

Vinylbutyrate

The monomer VB (Monomer Polymer Laboratories) was dried over anhydrous $MgSO_4$ and purified by fractional distillation. The fraction having b.p. 116.8–117°C, and refractive index $n_D^{20} = 1.4113$ was used.

tert.-Butylalcohol (TBA)

The solvent TBA (Shell) was dried over molecular sieves (Type 5A) and used after bulk recrystallization ($n_D^{27} = 1.3842$).

α,α' -Azobisisobutyronitrile (AIBN)

The initiator AIBN (Fluka) was recrystallized from methanol before use.

Reaction Conditions

The copolymers were prepared at $62 \pm 0.1^\circ\text{C}$ and $36 \pm 0.2\text{ atm}$ in TBA with the radical initiator AIBN. These seemingly arbitrary reaction conditions have been chosen for the sake of comparison with our previous results on ethylene-VAc copolymerization¹. The total concentration of both monomers at the start of each reaction was 1.50 mol/dm^3 , while the initiator concentration varied between 3.0 and 4.25 mmol/dm^3 . When the copolymerization had reached 40–50% conversion, the pressure was released and the reaction mixture was collected in a flask containing some inhibitor (hydroquinone). The precipitation of the copolymer was carried out in a water-methanol (9:1) mixture. After dissolving in acetone and filtration of the solution the copolymer was reprecipitated. The copolymer was then dried under vacuum at 40°C for several days. The homopolymers, PVAc and PVB, were synthesised and worked up under the same conditions.

Gaschromatographic Analysis

During the entire course of the copolymerization the reaction mixture was analyzed for monomer feed composition by the gaschromatographic method as reported by German and Heikens^{1,10}. The relevant gaschromatographic conditions were: column temperature, $80 \pm 0.1^\circ\text{C}$; stationary phase, 15% by weight of a mixture of diglycerol and quadrol (30–70% by weight) on chromosorb P, 60–80 mesh (Johns Manville).

Thermogravimetric Analysis

The weight of the samples was recorded as a function of the temperature by a Dupont 950 thermogravimetric analyzer. The heating rate was 15°C per min in all cases and a constant nitrogen flow was led over the sample. All samples analyzed weighed about 10 mg. The average ratio of weight loss over initial weight of three to five observations was determined in order to calculate the mole fraction VAc in the copolymer sample.

Results and Discussions

Two independent methods for the determination of the composition of VAc (1) – VB (2) copolymers will be discussed separately.

Gas Liquid Chromatography

By means of gas-liquid chromatography (GLC) the monomer feed composition of a reaction mixture can be followed during the copolymerization reaction. From this information the mean composition of the copolymer formed can easily be calculated as:

$$F = \frac{100(q_0 - q_e) + q_e f_2}{100(q_0 - q_e) + (q_e + 1)f_2} \quad (1)$$

where:

- F = mol-fraction VAc in the copolymer,
 q_0, q_e = quotient of the number of moles of VAc and VB in the reaction mixture at the start and the end of the reaction, respectively,
 f_2 = conversion of VB (M_2) in percent.

For all six samples investigated the mol-fractions (F) were calculated in this way. From Tab. 1 it becomes evident that VB is slightly more reactive than VAc, since the mol-fraction VB in the copolymer is higher than in the reaction mixture. These findings are in accordance with the conclusion reached in our kinetic investigation aimed at highly accurate determination of monomer reactivity ratios, yielding $r_1 = 0.893$ and $r_2 = 1.053$ under the conditions mentioned. These results, along with r -values and monomer reactivity-structure relations for other binary combinations of vinyl esters, will be published separately. The average homogeneous block lengths of VAc ($\bar{l}_1 = r_1 \cdot q_0 + 1$), and VB ($\bar{l}_2 = r_2/q_0 + 1$) varied from 1.36–4.57 and 3.61–1.26, respectively, for the different samples.

Thermogravimetric Analysis

The thermal stability of many polymers and copolymers has been studied by both isothermal and dynamical thermogravimetry. A quantitative analysis of some polymer blends¹¹ and copolymers^{6, 7} has been performed successfully with these techniques. Chiu⁶ reports that for copolymers these methods are based on the difference between the thermal stability of the various segments in the polymer chain. Dynamic thermograms of this type of copolymers result in the registration of two separately distinguishable and characteristic decomposition temperature stages, or the occurrence of one decomposition stage assignable to a single abstraction reaction. An example of the latter

Tab. 1. Results of the gaschromatographic analysis of the copolymerization of vinylacetate (1) and vinylbutyrate (2).

No.	Initial monomer feed position q_0	Final monomer feed position q_e	Conversion f_2 (%)	Initial VAc in the reaction mixture (mol-%)	Average VAc in the copolymer F · 100 (mol-%)	Average homogeneous block length $\bar{i}_1$	$\bar{i}_2$
1	0.402	0.415	37.5	28.7	27.4	1.36	3.61
2	0.659	0.688	49.1	39.7	38.6	1.59	2.60
3	1.070	1.110	37.0	51.7	50.0	1.96	1.98
4	1.510	1.575	44.0	60.2	58.8	2.35	1.70
5	2.355	2.480	44.0	70.2	68.7	3.10	1.45
6	3.996	4.289	56.6	80.0	79.0	4.57	1.26

case is the compositional analysis of ethylene-VAc copolymers, where the relative weight loss around 325°C turns out to be proportional to the weight-fraction VAc present in the copolymer⁷.

A completely different, and for random copolymers more general situation^{6,12} is encountered in the present case of VAc-VB copolymers. These are also shown to give rise to one acid abstraction stage as displayed in Fig. 1. Here, however, acetic and butyric acid are found to be abstracted simultaneously within the same small temperature interval (310–360°C).

Fig. 1. Typical dynamic TGA scan of a vinylacetate-vinylbutyrate copolymer containing 49.8 mol-% vinylacetate.

The compositional analysis of this copolymer is based on the assumption that the weight loss per mol "monomer unit", (ΔG) is intermediate to the losses *a* and *b* observed for the respective homopolymers, and linearly dependent on the composition *F* (mol-fraction VAc): $\Delta G = F \cdot a + (1 - F) \cdot b$. Combination with the expression for the total weight per mol "monomer unit": $G = F \cdot M_{VAc} + (1 - F) \cdot M_{VB}$ leads to the experimentally accessible quantity:

$$\frac{\Delta G}{G} = \frac{F \cdot a + (1 - F) \cdot b}{F \cdot M_{VAc} + (1 - F) \cdot M_{VB}} \quad (2)$$

where:

ΔG = weight loss of the sample,

G = weight of the sample,

M_{VAc} , M_{VB} = molecular weights of VAc and VB, respectively,

a , b = weight loss observed for one mol "monomer unit" PVAc and PVB, respectively.

In the case of complete acid abstraction, unbiased by average molecular composition and homogeneous block lengths, the parameters a and b should be equal to the molecular weights of acetic and butyric acid, respectively. In the present investigation the parameters a and b were determined from dynamic TGA measurements on the relevant homopolymers.

From Tab. 2 it can be seen that about 96% of the theoretically expected weight loss has been observed for both homopolymers. The order of magnitude of this degree of acid abstraction for PVAc has been confirmed by several authors^{8,12,13}. Servotte and Desreux¹² showed that the degradation products contained 90–95% acetic acid, when PVAc was degraded up to 70% by weight, and Mihai et al.¹³ observed 94% of the theoretically expected amount of acetic acid. On the other hand, Varma and Sadhir¹⁴ recently reported a higher percentage of acid loss (99%), but unfortunately the way of determination of the weight loss from the observed dynamic thermograms was not reported. The explanations for a reduced amount of acetic acid are somewhat contradictory and still incomplete, because no sufficient data are available to decide whether the polymers and the conditions were comparable. Possibly the various data were influenced by a different degree of branching of PVAc at the methyl group of the acetate¹⁵, since the abstraction of such branches does not yield acetic acid:

Surprisingly, neither Chiu⁶ nor Terteryan et al.⁷ have mentioned a correction term for the partial liberation of acetic acid, in analyzing ethylene-VAc copolymers.

In the present investigation these corrections have been taken into account. Furthermore, application of Eq. (2) implies the supposition that for both monomer segments the deviations from complete acid abstraction are indepen-

Tab. 2. TGA-results of PVAc and PVB.

Homopolymer	$\Delta G/G$ theoretical	$\Delta G/G$ experimental	Deviation from theor. $\Delta G/G$ (%)	Constant terms	Molecular weights of the aliphatic acids	Decomp. temp. (°C)
PVAc	0.698	0.670	3.95	a = 57.68	60.05	336.5
PVB	0.772	0.740	4.13	b = 84.46	88.10	340.5

dent of the mean chain composition and homogeneous block lengths, i.e. a and b are considered to be constants.

In Fig. 1 it is shown in which manner the mean decomposition temperature— $(t_1 + t_2)/2$ —and the weight loss (ΔG) of a copolymer sample are determined by applying an extrapolation method.

Tab. 3. TGA-results of the vinylacetate-vinylbutyrate copolymers.

No.	TGA			GLC
	Decomp. temp. (°C)	$\Delta G/G$	VAc in the copolymer (mol-%)	VAc in the copolymer (mol-%)
1	336.0	0.725	$26.5 \pm 0.6^*$	$27.4 \pm 0.3^*$
2	335.0	0.717	39.3 ± 0.6	38.6 ± 0.3
3	339.0	0.710	49.8 ± 0.6	50.0 ± 0.3
4	339.0	0.703	59.6 ± 0.6	58.8 ± 0.3
5	336.5	0.696	69.1 ± 0.6	68.7 ± 0.3
6	339.5	0.687	80.3 ± 0.6	79.0 ± 0.3

* Estimated standard deviations.

Examination of the results of Tab. 3 reveals that the mol-fractions calculated from TGA and GLC data agree satisfactorily. This may justify the conclusion that dynamic TGA is an accurate and rather rapid technique for compositional analysis of VAc-VB copolymers. Since the value of $\Delta G/G$ varies from 0.670 for PVAc to 0.740 for PVB it becomes evident that a slight error in this term (e.g. $0.5\% \approx 0.05 \text{ mg}$) shows up strongly in the mol-fractions to be determined (maximal 9%). Consequently, the average value of 3 to 5 observations is required in this dynamic TGA-method of analyzing VAc-VB copolymers.

A further extension of this analysis method to other vinylester (1) – vinylester (2) copolymers seems to be possible, because poly(vinylformate), poly(vinylpropionate), poly(vinylisobutyrate), poly(vinylmonochloroacetate) and poly(vinyltrifluoroacetate) have been shown to decompose¹⁶ at about the same temperature as PVAc, and probably, as suggested already by Gilbert et al.⁹, by the same reaction mechanism. Less TGA measurements will be necessary if the difference between the molecular weights of the monomers is large.

Conclusions

The above results of the compositional analysis of VAc-VB copolymers show that dynamic TGA, and GLC during the entire course of the copolymerization, yield identical results within experimental error, in spite of the fact that both monomer segments abstract their respective aliphatic acids simultaneously within the same temperature interval.

Although the acid abstraction is presumably incomplete, the accuracy of the method is independent of the composition and the average homogeneous block lengths of the copolymer chains.

Extension of this analysis method to other vinylester-vinylester copolymers seems to be promising.

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