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Identification of acrylate copolymers using pyrolysis and gas chromatography

Zbigniew Czech · Robert Pełech

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Abstract A combination of pyrolysis and gas chromatography were used to investigate thermal degradation products formed from acrylic copolymers containing alkyl acrylate and methacrylate. The method provided an analytical tool for characterizing the chemical composition and structure of the degradation products. Thermal degradation of the synthesized copolymers was analyzed using isothermal (250 °C) pyrolysis–gas chromatography. The degradation process, and the nature and amount of pyrolysis products, provides relevant information about the thermal degradation of acrylic copolymers and the mechanism of pyrolysis. During pyrolysis, the formation of corresponding olefins, alcohols, acrylates and methacrylate was observed.

Keywords Acrylic and methacrylic copolymers · Pyrolysis · Thermal degradation products · Analysis and identification

Introduction

Acrylate and methacrylate copolymers have excellent physical, chemical and mechanical properties. Such copolymers have many uses, for example as raw materials for adhesives, paints, varnishes and sealants in technical and medical applications [1, 2]. Copolymers based on acrylic or methacrylic acid esters and acrylic acid offer particular advantages, including excellent aging characteristics, resistance to elevated temperatures and plasticizers, and exceptional optical clarity due to polymer compatibility and non-yellowing. The thermal degradation behaviors of poly(acrylic acid) and acrylic copolymers with other unsaturated monomers have been examined in a number of studies [3–6] that have identified water and carbon dioxide as the main gaseous pyrolysis products. However, these volatile products cannot be used for accurate qualitative analysis of the copolymer degradation. Studies of the degradation of poly(acrylic acid) have revealed anhydride formation, indicating competition between dehydration and decarboxylation reactions. Quantitative analyses of the thermal degradation of poly(alkyl acrylates) have revealed products including alkenes, carbon dioxide, carbon monoxide and hydrogen [7]. The alcohols corresponding to the alkyl group are the major liquid products, with traces of monoacrylates and the corresponding methacrylates. All these products are accounted for in terms of radical reactions with a unique initiation step [8]. Pyrolysis–gas chromatography (Py–GC) can be used to easily, rapidly and inexpensively characterize polymer formulations as polymers or compound polymeric materials [9, 10]. The complex components of thermal degradation at high temperatures can be divided into three fractions: gaseous, liquid and residue. Heating of a sample in a closed system in an inert gas produces a pyrolysate that can be fed directly into a gas chromatograph, enabling identification of the constituent unsaturated monomers [11–13].

Experimental

Acrylic copolymers for the pyrolysis trials were synthesized from 97 wt% alkyl acrylate and 3 wt% acrylic acid (AA) in ethyl acetate, using 0.1 wt% AIBN as the radical starter. All monomers, AIBN and the organic solvent ethyl acetate were obtained from BASF, Germany.

Z. Czech (✉) · R. Pełech
Institute of Chemical Organic Technology, West Pomeranian University of Technology, Pułaskiego 10, 70-322 Szczecin, Poland
e-mail: psa_czech@wp.pl

The polymerization process was carried out under the following conditions: dosage time of residual monomers with residual AIBN, 1 h; time of post-reaction, 5 h; polymer content, 50 wt%.

The viscosities of the synthesized solvent-borne acrylic copolymers are listed in Table 1. For evaluation purposes an acrylic copolymer TEC MEB-2 from ChemCycle Bitterfeld GmbH, Germany comprising methyl acrylate (10 wt%), ethyl acrylate (20 wt%), butyl acrylate (30 wt%), 2-ethylhexyl acrylate (37 wt%) and acrylic acid (3 wt%) was used. The optimum conditions for pyrolysis of the acrylic polymers included a temperature of about 500 °C for 30 s in a helium atmosphere. The pyrolysis products of the acrylic copolymers were subject to gas chromatography under the following conditions: Intersmat IGC 131 gas chromatograph; QC2/BP1 capillary column (25 m × 0.25 mm; 100% dimethyl polysiloxane); He carrier gas (80 kPa); FID at 250 °C, injection temperature 250 °C, oven temperature program 50 (0 min) to 230 °C at 10 °C min^{-1} (32 min); injection volume 0.3 μL, and (Py–GC)/mass spectrometry techniques.

The pyrolysis apparatus was disassembled at the reduction union, and a 5 mg sample of acrylic polymer was placed in the bottom of the loop. The pyrolysis apparatus was reassembled and connected to the gas sampler valve instead of the constant volume tube. Plugs were placed in the regular sample inlet and in the vent openings of the gas sampler valve. Helium was used to flush air from the apparatus, and the system was closed. The loop of the apparatus was heated at 500 °C for 30 s. Products resulting from the pyrolysis were carried into the gas chromatography column using helium.

The identification and composition of the acrylic copolymers were determined by comparison of the sample pyrolysis chromatograms with chromatograms of known pyrolysis products of synthesized acrylic copolymers of known composition.

Results and discussion

Figures 1, 2, 3 and 4 show chromatograms of the thermal breakdown products of acrylic copolymers containing commercial alkyl acrylates and acrylic acid. The pyrolysis chromatogram of the acrylic copolymer based on methyl acrylate and acrylic acid (Fig. 1) contained three principal peaks representing methanol, methyl acrylate and methyl methacrylate, the latter corresponding to the acrylic acid methyl ester incorporated into the acrylic polymer chain. The pyrogram of the ethyl acrylate/acrylic acid copolymer showed ethanol, ethyl acrylate and ethyl methacrylate as the thermal degradation products. The peaks in Fig. 3 correspond to 1-butanol, butyl acrylate and butyl methacrylate. The presence of these three peaks in the pyrolysis chromatogram is possibly due to thermal decomposition of butyl acrylate groups in the side chain. The pyrolysis

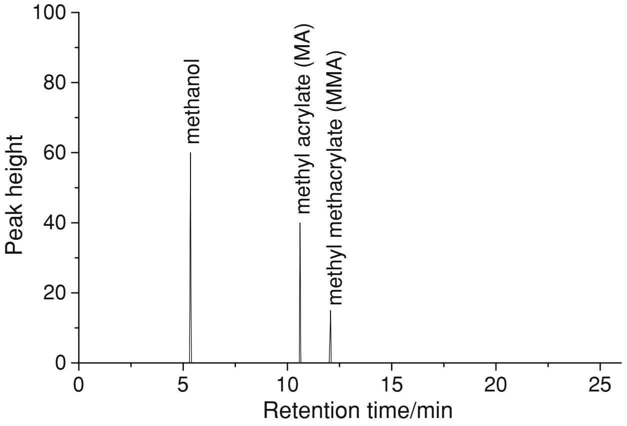

Fig. 1 Chromatogram of the pyrolysates of acrylic copolymer methyl acrylate-acrylic acid

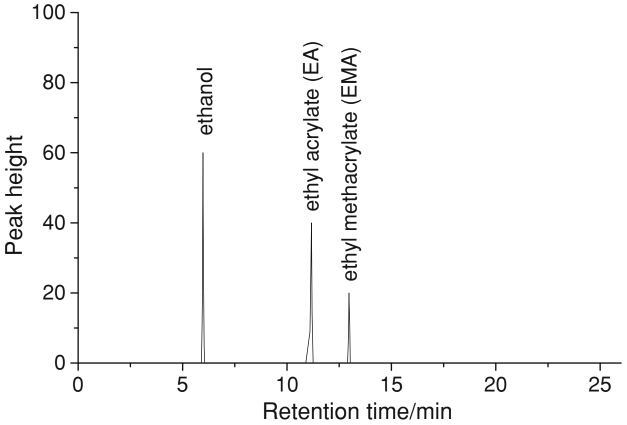

Fig. 2 Chromatogram of the pyrolysates of acrylic copolymer ethyl acrylate-acrylic acid

Table 1 Viscosity and composition of synthesized acrylic copolymers

Copolymer name	Alkyl acrylate (wt%)	Acrylic acid (wt%)	Viscosity (Pa s)
MA/AA	Methyl acrylate 97	3	7.3
EA/AA	Ethyl acrylate 97	3	6.0
BA/AA	Butyl acrylate 97	3	4.3
2-EHA/AA	2-ethylhexyl acrylate 97	3	2.8

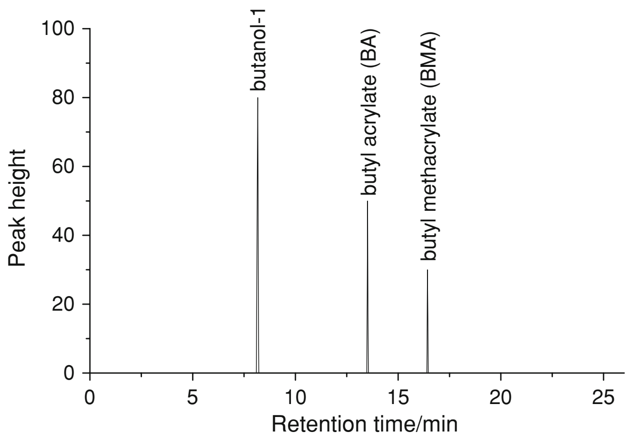

Fig. 3 Chromatogram of the pyrolysates of acrylic copolymer butyl acrylate-acrylic acid

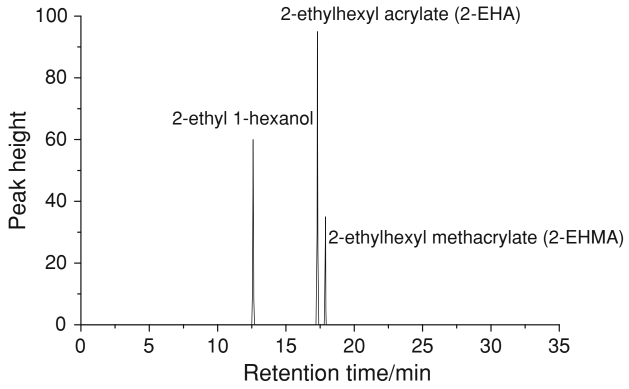

Fig. 4 Chromatogram of the pyrolysates of acrylic copolymer containing 2-ethyl hexyl acrylate and acrylic acid

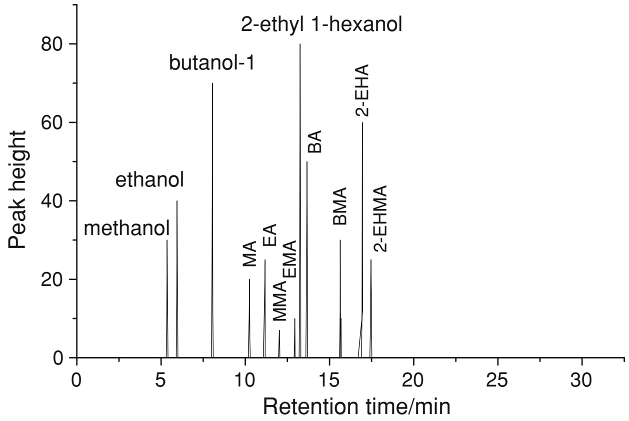

Fig. 5 Chromatogram of the pyrolysates of investigated acrylic copolymer containing commercial alkyl acrylates and acrylic acid

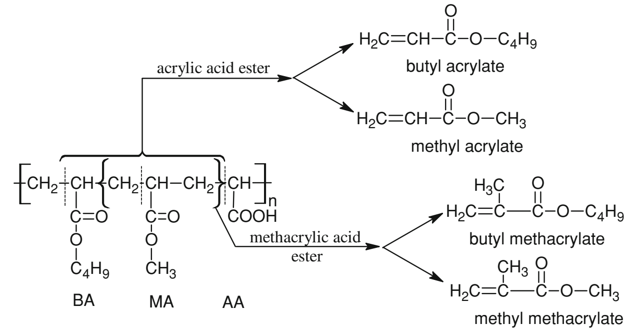

Fig. 6 Formation of acrylic and methacrylic monomers during the pyrolysis of acrylic copolymers

behavior of the acrylic copolymers is in good agreement with own trials in terms of the quantitative yield of 1-butanol, butyl acrylate and butyl methacrylate from the ester. As chain fragments from the copolymer based on 2-ethylhexyl acrylate and acrylic acid were also included, the corresponding monomers 2-ethyl 1-hexanol, 2-ethylhexyl acrylate and 2-ethylhexyl methacrylate were observed in the liquid phase. Figure 5 shows the chromatogram of the pyrolysate of an externally synthesized acrylic copolymer (TEC MEB-2) containing methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate and acrylic acid. Comparison of the retention times of the major peaks for various polymerizations using unsaturated acrylate monomers indicated the presence of four main monomers. The additional peaks present were accounted for by comparison with the chromatograms of individual polymers. The acrylic copolymer was identified as being composed of methyl acrylate, ethyl acrylate, butyl acrylate and 2-ethylhexyl acrylate. The mechanism of formation of the liquid breakdown products can be explained on the basis of the characteristic properties and thermal resistance of typical acrylic copolymers (Fig. 6).

Conclusions

Gas chromatography, coupled with a controlled-temperature pyrolysis technique, provided a rapid method for the identification of acrylate and methacrylate copolymers. Small samples of copolymers were pyrolyzed, and the pyrolysate was fed directly into a gas chromatograph using a gas sampling valve. Chromatography of the complete pyrolysate enabled separation and identification of higher boiling point substances, monomers and the esters of acrylic and methacrylic acid.

This gas chromatography method can also be used for the semi-quantitative determination of acrylate and methacrylate monomers in different mixtures of polymers. This technique may prove useful in solving problems associated with the production of acrylic polymers, and for the monitoring and analysis of commercial products containing developed and ready-to-use acrylic materials. The applicability of this method to the analysis of other types of polymers is being investigated.

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