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Pyrolysis GC-MS methods for studying the composition and dissolution behaviour of co-polymers

Introduction

Copolymers of vinylpyrrolidone (VP) and vinylacetate (VA) have good binding and film-forming properties, affinity to hydrophilic and hydrophobic surfaces, and a relatively low hygroscopicity. Therefore, such copolymers are widely used in pharmaceutical and cosmetics products.

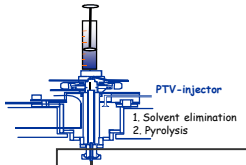
Properties of the copolymers strongly depend on the ratio of VP and VA. Solubility in water increases with increasing VP content in the copolymer. Py-GC-MS was used to study two commercially available products of this nature.

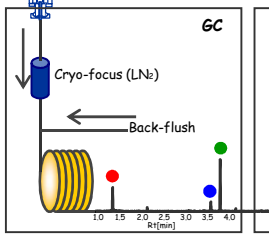
In this project we are developing methods for the qualitative (identification and determination of composition) and quantitative analysis of dissolved copolymers in water.

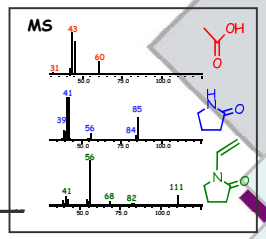
Experimental

All Py-GC-MS analyses were performed on a Shimadzu GCMS-QP2010plus instrument equipped with an Optic-3 PTV injector from ATAS GL. GC analyses were carried out on a 30 m x 0.25 mm i.d. TC 5MS (5% phenyl-methylpolysiloxane) column with a film thickness of 0.25 μm (GL Sciences) using helium as the carrier gas at the flow rate 2 mL/min. The PTV was programmed from 40°C to 130°C and after elimination of the solvent with 30°C / s to 600°C (optimized for all analyzed polymers). The GC temperature program started once the cryo-trap was heated, 2 min after the PTV-injector had reached the final pyrolysis temperature. The GC temperature program started at 60°C and ran to 320°C at 40°C/min. The mass spectrometer was used in the full-scan mode. Electron ionization mass spectra were obtained across the range of 40–500 Da at 70-eV electron energy.

Results



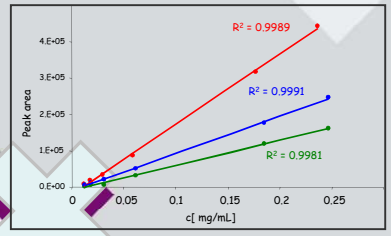




Schematic picture of the automated Py-GC-MS using PTV pyrolysis. 1 μL of a mixture of PVP and PVA dissolved in water/ethanol (1/1, v/v), was injected.

- Acetic acid
- 2-Pyrrolidinone
- N-vinylpyrrolidone

have been identified as pyrolysis products of blends of PVP and PVA, as well as of copolymers (PVP-co-VA). For identification MS library NIST147 was used.



Calibration curves of each pyrolysis product from blends of PVP (K25, M_R =24,000 Da) and PVA (M_R =12,800 Da), 1/1 (v/v), Repeatability for n = 3, RSD% < 4 %.

Molar ratios of VP/VA for PVP-co-VA were calculated using calibration curves obtained for the blend solution PVP + PVA (molar ratio of 51/49).

	Py-GC-MS %		Reference %		Difference %
	VP	VAc	VP	VAc	
Blend 1	66.7	33.3	65.4	34.6	1.3
Blend 2	50.8	49.2	50.1	49.9	0.7
Blend 3	34.0	66.0	32.1	67.9	1.9
Luviskol*VA37E	38.0	62.0	30.0	70.0	8.0
Luviskol*VA55I	55.5	44.5	50.0	50.0	5.5
Luviskol*VA64P	66.1	33.9	60.0	40.0	6.1
Plasdone*S630	64.5	35.5	60.0	40.0	4.5
Kollidon*VA64	65.9	34.1	58.6 - 64.7	35.3 - 41.4	1.2
Processed*VA64	64.7	35.3	58.6 - 64.7	35.3 - 41.4	0.0
Luviskol*VA73E	76.0	24.0	70	30	6.0

Comparison of experimental molar ratios of pyrolysis products with manufacturer-specified molar ratios of monomers.

Peak areas of acetic acid and N-vinylpyrrolidone were used to calculate the dissolution rate of co-polymers in water.

Conclusions

- Py-GC-MS was successfully applied to copolymers of vinylpyrrolidone (VP) and vinylacetate (VA)
- Using Py-GC-MS we can obtain chemical composition information on PVP-co-VA copolymers
- The method showed good performance in terms of repeatability and reliability
- Py-GC-MS is a suitable method for measuring dissolution rates of PVP-co-VA in water

References

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