THE THERMAL BEHAVIOUR OF ALKYLVINYLPHOSPHONATES- ACRYLATES COPOLYMERS

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Introduction

Importance:

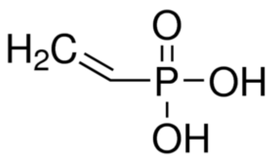
Copolymers of dialkylvinylphosphonates (alkyl=methyl, ethyl) were deeply studied and find application in the electrical, transportation and construction industries thanks to their properties such as flame-retardance, adhesion to metal oxides, anticorrosion properties, selective polymer sorbents and biomedical applications.

Aim

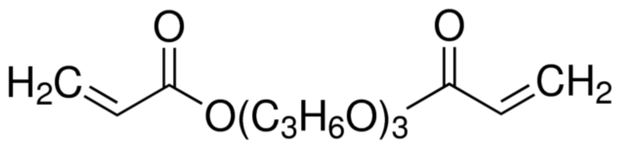
Copolymers of dialkylvinylphosphonic acid esters: dimethylvinylphosphonate (DMVP) with tri(propylene glycol) diacrylate (TPGDA) at different molar ratios from 1:1 to 5:1 were obtained by using UV light and photoinitiator. The behavior of a series of copolymers DMVP:TPGDA containing phosphonated groups regarding thermal degradation and flammability has been investigated by thermal analysis (TGA) and limited oxygen index (LOI).

Experimental

Photopolymerizable formulation contains:
-monomer: dimethylvinylphosphonate (DMVP)



-tri(propylene glycol) diacrylate (TPGDA)



-photoinitiator: Darocure 4265, 3% w/w vs monomer

Methods: The formulations DMVP: TPGDA 1:1 to 5:1 with 3% photoinitiator, were laid on PTFE plates and cured using a medium vapour pressure mercury lamp SUNRAY400 with light intensity of 30 W.cm^{-2}.

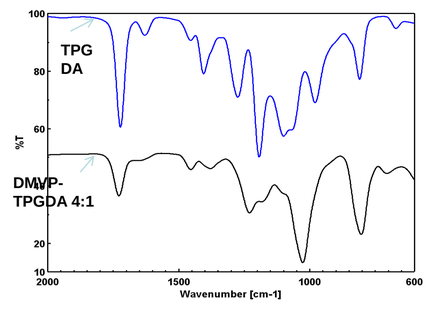
Conclusions

•The use of UV light is an efficient and advantageous technique to obtain copolymers from dimethylvinylphosphonate (DMVP) and tri(propylene glycol) diacrylate (TPGDA). The copolymers are insoluble in water or in common solvents.
•These (co)polymers showed good LOI values (in the range 26-30).
•The presence of the phosphonate group reduces flammability of the polymers.

Results and discussion

Characterization of polymers

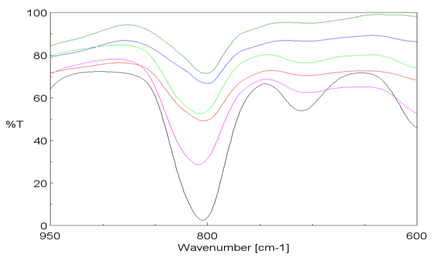
- ATR-FTIR spectra was performed by spectrometer Jasco FTIR 4200, ZnSe crystal plate;
- thermal analysis was performed by TGA/SDTA 851-LF 1100-Mettler Toledo, in air, in the range of temperature 25-650 ^{0}C, heating rate 10 ^{0}C/min.



FTIR ATR spectra of TPGDA and copolymer DMVP-TPGDA 4:1

Characteristic bands of monomers and copolymers

C=O	1724-1727 cm-1
P=O	1265-1229 cm-1
P-O-CH3 phosphonate	1090-1026 cm-1
C=C	1727-1722 cm-1
P-C	785-680 cm-1
P-O-C (streching)	803-809 cm-1



ATR FTIR spectra of polymers DMVP:TPGDA. Dependence of intensity of P-O-C stretching band on DMVP molar ratio in copolymer.

Characterization of polymers

Polymer	Tmelt	T5% °C	T10% °C	T50% °C	residue at 650 °C, %	LOI %
DMVP : TPGDA 1:1	72.4	175.2	261.0	325.6	13.28	26
DMVP : TPGDA 2:1	62.0	138.8	256.5	315.2	13.03	27
DMVP : TPGDA 3:1	68.3	144.3	261.4	324.0	15.41	27
DMVP : TPGDA 4:1	67.8	152.4	268.0	354.0	17.90	29
DMVP : TPGDA 5:1	74.0	178.1	270.2	362.6	20.96	30

Char formation is important to flame retardancy because the carbonaceous char formed during degradation on the top of a polymer can protect the underlying polymer from exposing to the flame. Char yield at 650^{o}C is higher in the case of DMVP : TPGDA 5:1 and it is related to the phosphorus percent in unity of mer. This indicates an improvement of flammability of copolymers.
LOI measurements indicated their potential application as fire retardant materials being a precision method for determining the relative flammability of various materials by measuring the minimum concentration of oxygen required to support combustion. Limiting oxygen index (LOI) was determined on the powdered sample in according to modified ASTM D2863-70. These polymers show LOI values in the range 26-30, comparable with other polyphosphonates and polyphosphates.
The presence of the phosphonate group reduces flammability of the polymers.

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