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The synthesis of MMA-S copolymer starting from PMMA and elemental sulfur

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SUMMARY

The synthesis of methylmethacrylat (MMA) - sulfur copolymer has been completed by starting from a mixture of Polymethylmethacrylat (PMMA) and elemental sulfur at high pressure (10000 Kgf/cm^2) and high temperature (350'C) by using a specially designed reaction vessel. The formation of copolymer is spontaneous and is due to the presence of active species (free biradical of MMA and S) generated through the decomposition of PMMA and polysulfur under extreme conditions.

The resulted copolymer has been characterized by using elemental analysis, IR, NMR and MS spectroscopy.

INTRODUCTION

Copolymerization occurs between almost any pair of polymerizable vinyl monomers, and also between one monomer which does homopolymerize and other which does not, and can also occur when neither monomer homopolymerizes readily. Copolymers are of great importance since it is possible to make significant changes in the physical properties of a finished polymeric material simply by changing the nature and the amount of the comonomers. This is the reason why new methods of obtaining copolymers and new copolymeric structures present a special interest both for academic and applicative investigations.

Enikolopian and coworkers reported many years ago some synthesizes of obtaining polymeric materials at high pressures by starting from usual monomers [1]. Polyacrylamide has been synthesized for instance at 10–20 Kbars. The formation of some copolymers has also been presented by using homopolymers (polyformaldehide and polydioxolane) and various catalytic systems under common conditions [2].

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In this paper a new way is suggested for synthesizing polymeric materials under extreme conditions, by starting from homopolymers and / or from mixtures of them, which undergo thermal depolymerization (with long kinetic chain).

Table I. Heat induced monomer formation (half-life of 30 min.) of polymers in absence of air

Polymer	Monomer Fraction mol %	Temperature (C)
Poly-α-methyl styrene	100	-
Polyoxymethylene	100	-
Polytetrafluorethylene	96	510
Polymethylmethacrylate	95	330
Polymethacrylonitrile	85	-
Polystyrene	41	360
Polyisobutene	20	350

The importance of depolymerizations during thermal degradations becomes evident from the monomer release (in volatile products) of various polymers in absence of air [3-4] (table I).

Meeting the proper thermodynamic conditions, for the native monomer molecules, resulted under thermal depolymerization mechanisms in the absence of air, new highways open up for recombination processes, which could lead eventually to the appearance of polymeric and copolymeric structures.

The present paper reports specifically the synthesis of MMA - S copolymer under the above mentioned circumstances.

EXPERIMENTAL

Materials

Emulsion polymerization (1 μm diameter) PMMA beads and pure native sulfur were used as starting materials.

The copolymerization reaction were carried out in a specially designed, thermostated reaction vessel presented in figure 1. The main components of the reactor (hollow cylinder 9, piston 10 and pressing pellets 2, 4 and 6) are built up of hard steel, to support pressures as high as 10000 kgf/cm^2 and temperatures up to 450'C. The mixtures of starting materials are placed between the pressing pellets 4 and 6 and the advanced sealing for high pressure condition is assured by the aluminum O-rings 3 and 7. The mantle 8 allow a controlled and uniform heating up of the system, permitting at the same time, through channel 1 the degassing of the starting products before initiation of the copolymerization reactions.

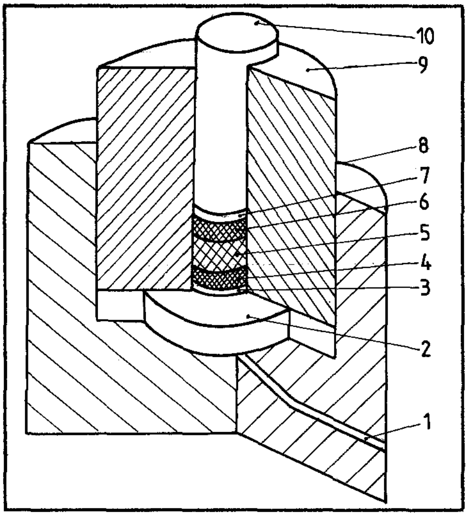


Figure 1. The thermostated reaction vessel (unconventional conditions). 1-channel; 2,4,6-pressing pellets; 3,7-aluminum O-ring; 5-mixture of starting materials; 8-mantle; 9-hollow cylinder; 10-piston.

Copolymerization

The copolymerizations were carried out by using degassed mixtures of PMMA and sulfur, at 10000 kgf/cm^2 (by using a SPECAC 15 tons hydraulic press - UK) and at 320'C. In a typical experiment the mixture of PMMA and S (MMA / S = 3/1) is introduced between the pressing pellets 4 and 6, then the selected pressure is established and the temperature is raised, in a couple of minutes, to the copolymerization value. The isothermal condition is maintained for the reaction period (30 minutes), followed by the slow cooling down of the system. The brown colored, solid phase final reaction product is released from the reaction device eventually.

Analytical instruments used for the characterization of the copolymers

The IR (KBr pellets) and UV ($CHCl_3$ solution; reference $CHCl_3$; cuvettes with path length 10 mm) spectra were recorded on PERKIN ELMER 577 spectrometer. The NMR ($CDCl_3$ solution) spectra were obtained by using a JEOL C60 HL (60 MHz) instrument. Various temperature mass spectra were recorded (solid sample holder device) on a MAT-111 VARIAN instrument. Elemental analysis were carried out in order to compare the relative ratio of the elements of the starting materials and the final reaction product. The thermal properties (TG and DTA curves) of the parent polymer and copolymer were monitored by using MOM - Derivatograph instrument.

Table II. The Comparative elemental analysis data of standard PMMA and of P(MMA-S)

Elem.	PMMA		P(MMA-S)	
	%	Stoich.	%	Stoich.
C	60.0	5	56.96	4.98
H	8.0	8	7.47	7.84
O	32.0	2	30.48	2.00
S	-	-	5.09	0.17

RESULTS AND DISCUSSIONS

The elemental analysis data (table 2) points for a 1S / 6MMA ratio composition copolymer when the S / MMA value in the starting "monomer" mixture is 1/3.

The IR spectrum of P(MMA-S) copolymer in comparison to that of standard PMMA are presented in figure 2.

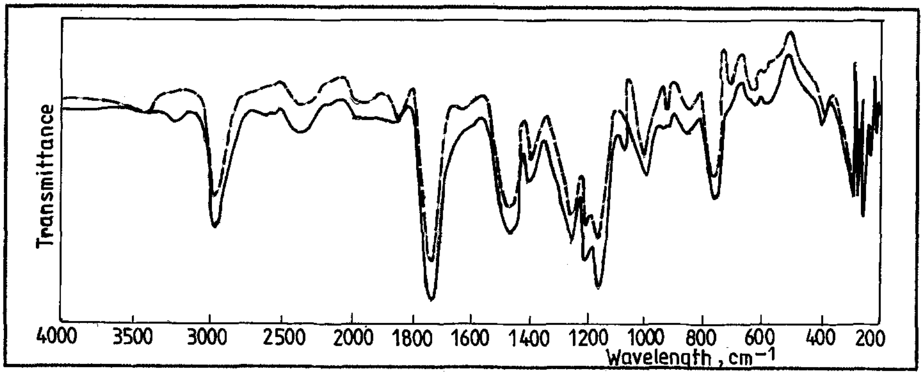
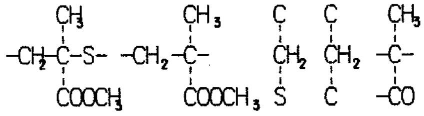


Figure 2. The IR spectra of the PMMA and the P(MMA-S)

It can be noticed that the spectra of PMMA polymer and P(MMA-S) copolymer are practically the same, due to the fact that the C-S (700-600 cm^{-1}), S-S (500-400 cm^{-1}) and similar linkages are not readily identified because either the absorption is extremely weak or the position of the band is too variable. On the other hand the S-H absorption (2600-2550 cm^{-1}) is not inherently strong and whilst it is usually well defined, it is often difficult to detect in samples containing -COO- groups which exhibit general absorption in this region [5].

The H-NMR spectrum (fig. 3) of the chloroform soluble fraction (7 % of the copolymer) of the P(MMA-S) raw reaction product shows characteristics signals due to the presence of the structural units:



$$\begin{array}{ccccc} -CH_2-\underset{COOCH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-S- & -CH_2-\underset{COOCH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}- & \begin{array}{c} C \\ | \\ CH_2 \\ | \\ S \end{array} & \begin{array}{c} C \\ | \\ CH_2 \\ | \\ C \end{array} & \begin{array}{c} CH_3 \\ | \\ -C- \\ | \\ -CO \end{array} \end{array}$$

(A) (B) (C) (D) (E)

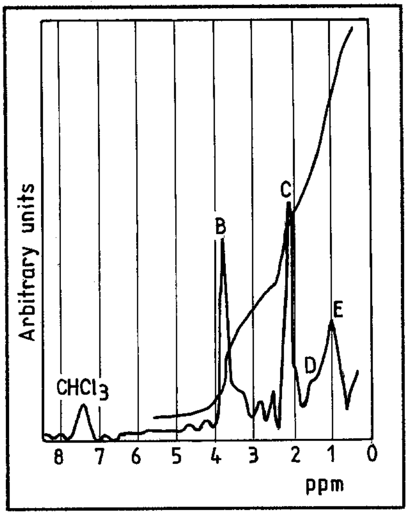


Figure 3. The H-NMR spectrum of the P(MMA-S) copolymer.

The estimated A and B percent composition of the copolymer is 25% and 75% respectively.

The mass spectra of the copolymer were recorded at various temperatures (180'C, 250'C and 310'C) of vaporization.

It is noteworthy that all of the spectra exhibit both molecular fragments of MMA and its sulfur derivatives and that the sulfur containing fragments proportion increases with the increase of the volatilization temperatures.

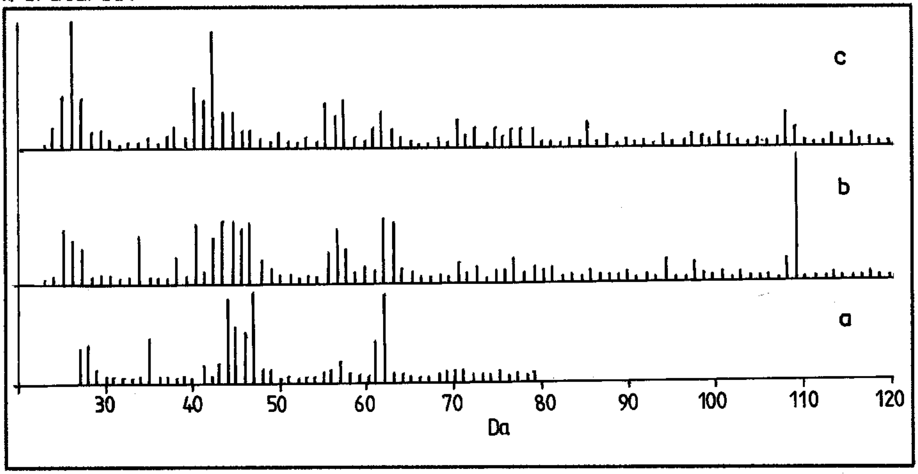


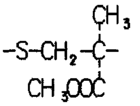
Figure 4. The Mass spectra of the P(MMA-S) copolymer recorded at various temperatures of vaporization (a-80'C, b-250'C, c-330'C)

Molecular monomers units appear at low intensities in the spectra, because of the development of intense fragmentation processes during the analysis. Table III presents the molecular fragments of MMA and of its sulfur derivatives identified in the MS spectra.

Table III. Comparative molecular fragments of MMA its sulfur derivatives

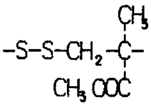
MMA			S-MMA		S-S-MMA	
Molecular fragment	Mw	%	Molecular fragment	Mw	Molecular fragment	Mw
$H_2C=C(CH_3)$ $COOCH_3$	100	34	$HC=C(CH_3)$ $HS\ COOCH_3$	132	$HC=C(CH_3)$ $HSS\ COOCH_3$	164
$H2C=C(CH_3)$	41	100	$HC=C(CH_3)$ HS	73	$HC=C(CH_3)$ HSS	105
$H2C=C(CH_3)$ CO	69	66	$HC=C(CH_3)$ $HS\ CO$	101	$HC=C(CH_3)$ $HSS\ CO$	133
$H2C=C=CH$	39	40	$HC=C=CH$ HS	71	$HC=C=CH$ HSS	103
$H2C=C=CH_2$	40	10	$HC=C=CH_2$ HS	72	$HC=C=CH_2$ HSS	104

The MS data allow to suggest the presence in the copolymer chains the following structural units:



$-S-CH_2-\underset{CH_3OOC}{\overset{CH_3}{C}}-$

(101; 73; 72; 71)



$-S-S-CH_2-\underset{CH_3OOC}{\overset{CH_3}{C}}-$

(133; 105; 104; 103)

The TG and DTA curves are presented in figure 5. The decompo-sition mechanism of P(MMA-S) copolymer in comparison to that of the PMMA (depolymerization with long kinetic chain) shows three processes due probably to the sulfur atoms presence within the macromolecular chains.

CONCLUSIONS

These findings suggest that in extreme conditions starting with a mixture of PMMA and elemental sulfur P(MMA-S) copolymers arise with structural units of A and B. The insoluble part of the copolymer can be explained by crosslinking processes probably.

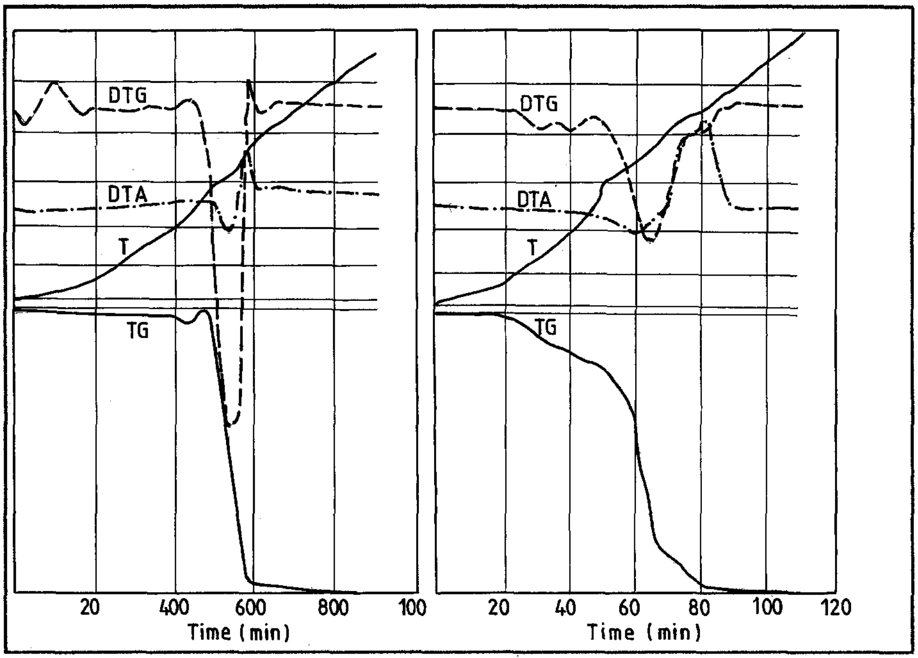


Figure 5.The Thermal properties of the PMMA (a) and of the P(MMA-S) copolymer (b).

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