

SYNTHESIS OF BLOCK COPOLYMERS WITH TETRAPHENYL BIPHOSPHINE INIFERTER

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ABSTRACT

In this study PS/PMMA block copolymers were synthesized from polystyrene – (PS-) with active aromatic phosphorous end groups as macroinitiator using UV light as the energy source. The yield of block copolymerization of styrene and methyl methacrylate (MMA) with PS-macroinitiator in bulk was determined in relation to the wavelength of UV light and on the ratio of initiator and monomer. The molecular weights of block copolymers increased with the increase of the reaction time. It was found out that block copolymerization of styrene and methyl methacrylate with PS-macroinitiator gives higher yields at the wavelength of 302 nm than at 366 nm. The macroinitiators decomposed into phosphorous radical and macroradical. The macromolecules were terminated by primary $\text{Ph}_2\text{P}\bullet$ radicals and by the combination of two equal or different macroradicals as observed by NMR spectroscopy. The quantities of homopolymers and block copolymer in our products were determined by solid-fluid extraction.

INTRODUCTION

Modern materials research is oriented towards living polymer systems which allow for more control over the mechanism of polymerization. This mechanism also gives narrow molecular weight distributions of polymer products which has a direct influence on the mechanical properties of materials. The mechanism of living polymerization was first described by Szwarc [1] for anionic polymerization and afterwards for cationic polymerization. There has been a lot of research focussing on radical living polymerization which allows for a wide selection of monomers, solvents and higher

† Dedicated to the memory of Prof.Dr. Anton Šebenik

temperatures [2]. Otsu [3] first described living radical mechanism, suggesting the important role of the iniferter in the polymerization process (the term iniferter is a combination of **in**itiator, **trans**fer agent and **ter**minator). Iniferters containing bonds with low decomposition energy, such as S-S or P-P bonds, can be used.

Pseudoliving radical polymerization was defined by Harwood [4] as a reaction between monomers and initiators in which polymers with active end groups are formed. These polymers can further be used as macroinitiators for the second step of polymerization with the same, or other monomers, to form block copolymers.

Our work focused on the controlled synthesis of polystyrene macroinitiators (PSMI) in bulk using tetraphenyl biphosphine (Ph_4P_2) iniferter. PSMI were further used in block copolymerization with methyl methacrylate to form PMMA-PS-PMMA block copolymers. The active end group bonding and an increase in molecular weight and polydispersity were determined.

EXPERIMENTAL

Materials: Tetraphenyl biphosphine (Ph_4P_2) (product of Aldrich) was used as the initiator. Substances methyl methacrylate (MMA) and styrene (S) were products of Rohm and Haas. Monomers were washed with a 10% solution of sodium carbonate and distilled water, dried over night with nonaqueous sodium sulphate, and distilled twice under reduced pressure. Monomers were used immediately after the purification. All solvents were dried, purified and distilled twice in dry argon atmosphere to remove all oxygen.

Polymerization: Polymerization of substances was carried out in two steps in a dry box with argon atmosphere with the content of oxygen below 1 ppm. In the first step, the PS-macroinitiators were synthesized. The monomer was mixed in a quartz reaction vessel with the selected quantity of a Ph_4P_2 initiator (Table 1). The initiator concentration was between 0.035 and 1.050 mol/dm³ (molar ratio monomer to initiator 1:0.0001 to 1:0.003). The energy sources for polymerizations were UV lamps of 302 and 366 nm wavelength with the intensity of 4.5 mW/cm² at 2.5 cm distance. The reaction temperature was 25°C and the polymerization time between 1 and 4 h. At individual reaction time intervals, the samples for determining the molecular weight and

yield of the polymerization were withdrawn from the reaction vessel. After the polymerization, the PS macroinitiators were purified by precipitating a THF solution by methanol (ratio 1:10) at room temperature in the dry box. Precipitation was repeated three times to remove the unreacted initiator and monomer. Following this, the products were dried in argon atmosphere.

To evaluate the degree of photopolymerization, two control experiments without Ph_4P_2 under the same reaction conditions were carried out. The control experiments for thermal polymerization with Ph_4P_2 and without UV irradiation were carried out as well.

Block copolymerization: In the second step of polymerization, some selected purified polymers were used as macroinitiators for the synthesis of block copolymers. The macroinitiator was dissolved in MMA as a 1 wt % to 10 wt% solution, and then irradiated. The reaction conditions were the same as for the synthesis of macroinitiators. After the polymerization was quenched, the block copolymers were precipitated and dried. [2,5]

Measurements: The structure, configuration of chain end groups, purity and the presence of unreacted initiator were followed by NMR spectroscopy of the polymers. The ^1H , ^{13}C and ^{31}P spectra were measured with Bruker AVANCE DPX-300 MHz NMR spectrometer in one and two dimensional techniques with homo and hetero correlation. The samples were dissolved in CDCl_3 , and NMR tubes fused in a dry box with argon atmosphere to prevent oxidation of phosphine end groups. All signals were quoted on TMS as internal standard and H_3PO_4 was used as an external standard. The molecular weights were measured by GPC using PL-gel columns with pore sizes of 50 nm, 100 nm and 1000 nm and THF as the eluent (1ml/min). PS standards were used for column calibration for PSMI samples; similarly, PMMA standards were used for block copolymers (such as for PS/PMMA where the shorter PS block is surrounded by longer PMMA blocks at both sides).

RESULTS AND DISCUSSION

Yield of polymerization: As shown in Table 1 the yield of polymerization is higher at 366 nm wavelength than at 302 nm in polymerization of styrene with Ph_4P_2 . On the other hand, block copolymerization of the polystyrene macroinitiator and methyl

methacrylate gives much higher yields at 302 nm wavelength than at 366 nm in spite of shorter polymerization time (Table 2). The UV spectra of the initiator and macroinitiators show that these absorb light at higher wavelengths than styrene. At the wavelength of 302 nm part of the energy is absorbed by styrene which leads to the formation of a reduced number of primary radicals [6] and thus results in a smaller conversion.

Table 1: Bulk polymerization conditions of styrene with Ph₄P₂

Experiment	Quantity of Ph ₄ P ₂ /g	λ /nm	Polymerization time/h	Quantity of O ₂ /ppm	Yield of polymerization/%
1	0.037	366	4	0.4	11.1
2	0.071	366	4	0.3	9.9
3	0.109	366	4	0.3	9.1
4	0.204	366	4	0.4	7.1
5	0.218	366	4	0.6	6.9
6	1.095	366	4	1	6.8
7	0.364	366	4	0.6	11.8
8	0.110	366	7	1	14.0
9	0.216	366	7	1	15.9
10	0.353	366	7	0.3	7.9
11	0.358	302	4	1.5	5.5
12	0.357	302	4	0.1	6.3
13	0.374	302	4	1	4.9
14	0.364	302	4	0.9	4.2

Considering the literature data [7] and our data obtained by calculation using the molecular orbital theory [8], we found the C-P bond dissociation energy to be up to 152 kJ/mol with bond lengths above 0.175 nm. The P-P bonds are longer (0.23 nm) and have smaller dissociation energy compared to C-P bonds. In the synthesis of block-copolymers the wavelength 366 nm has insufficient energy for the dissociation of C_{alif}-P bonds. Therefore the wavelength of 302 nm is more appropriate. This explains why the

yield of the synthesis of PSMI is higher at wavelength 366 nm while higher yields of block copolymerization of PSMI and MMA occur at 302 nm.

Table 2: Bulk polymerization conditions of methyl methacrylate with PSMI

Experiment	Quantity of PSMI/g	λ /nm	Polymerization time/h	Quantity of O ₂ /ppm	Yield of polymerization /%
1	0.697	366	4	0.6	12.6
2	0.204	366	4	0.8	7.07
3	0.341	366	4	2.5	12.5
4	1.055	366	4	2	17.6
5	0.648	366	4	2	20.9
6	1.050	366	4	2	22.8
7	0.111	366	4	1	10.7
8	0.450	366	4	1.2	12.2
9	0.108	366	4	0.5	7.6
10	0.200	366	4	1.2	13.7
11	0.263	302	2	0.1	53.2
12	0.226	302	2,5	1.6	100
13	0.221	302	2	1.4	64.9
14	0.233	302	2	1.6	42.3

Quantities of homopolymers and block copolymers in products: One evidence of the proofs of living polymerization is the ability of the macroinitiator to initiate the second step of polymerization. For this reason we used the PS macromolecule with two active end groups as a macroinitiator synthesized during the first step of polymerization for the synthesis of block copolymers. In this case, UV irradiation decomposed the C_{alif}-P bond into a macroradical and a primary radical. The reactivity of macroinitiator was confirmed by an increase in molecular weight, from 9800 g/mol (the first step) to 250000 g/mol (the second step) at wavelength 366 nm and from 5000 g/mol to 155000 g/mol at 302 nm (Table 3).

Table 3: Number-average molecular weights for PSMI ($M_n(1)$) and block copolymers ($M_n(2)$), the results of solid-fluid extraction and quantities of PS/PMMA block copolymers and homopolymers after the second step

Exp. No.	$M_n(1)$	$M_n(2)$	M_w/M_n PS/PMMA	λ/nm	Reaction time /h	PS /%	PMMA and PS/PMMA /%
9	7000	140000	1.75	366	4	11.39	83.92
7	9800	250000	1.71	366	4	11.45	88.29
14	4500	138000	1.54	302	2	0.02	96.33
4	5000	155000	1.51	302	2	0.31	96.88

To determine whether a homopolymer was formed during the second step of polymerization, the block copolymers were successively extracted with cyclohexane (for PS) and with acetonitrile (for PMMA and for PS/PMMA block copolymers). All extractions were carried out in Soxhlet [9] apparatus for 10 hours. The results of the extraction for samples of block copolymers PS/PMMA, prepared with different quantities of the initiators in the first step and different quantities of PS-macoinitiators in the second step, are given in Table 3. It can be seen that the primary radicals formed from the macoinitiators terminated the block copolymers chain growth and also initiated homopolymerization of MMA. From the extraction data (Table 3), the share of unreacted PS-macoinitiators was found to be between 0.3% at wavelength 302 nm and 11% at wavelength 366nm. We believe that 96% of the product at wavelength 302 nm and 88% of the product at wavelength 366 nm is a mixture of PMMA homopolymer and PS/PMMA block copolymer, since PS/PMMA is also soluble in acetonitrile, because of a very small short PS block in comparison with the PMMA block.

Chain end-groups: The determination of the polymer chain end-groups is a useful way of studying polymerization mechanism. The most appropriate method is high resolution 1H and ^{31}P NMR spectroscopy. NMR spectra interpretation [10,11,12] is given for the sample PSMI No. 14, which was further used for block copolymerization with MMA. In ^{31}P NMR spectra of PSMI (Figure 1) peaks close to -20 ppm represent polystyrene with diphenyl phosphine (Ph_2P) end groups in head and tail forms. The two dimensional NMR spectrum (Figure 2) shows bonding of polystyrene with diphenyl phosphine end group in the tail form at 7,2 ppm and in the head form at 7,0 ppm on the proton scale.

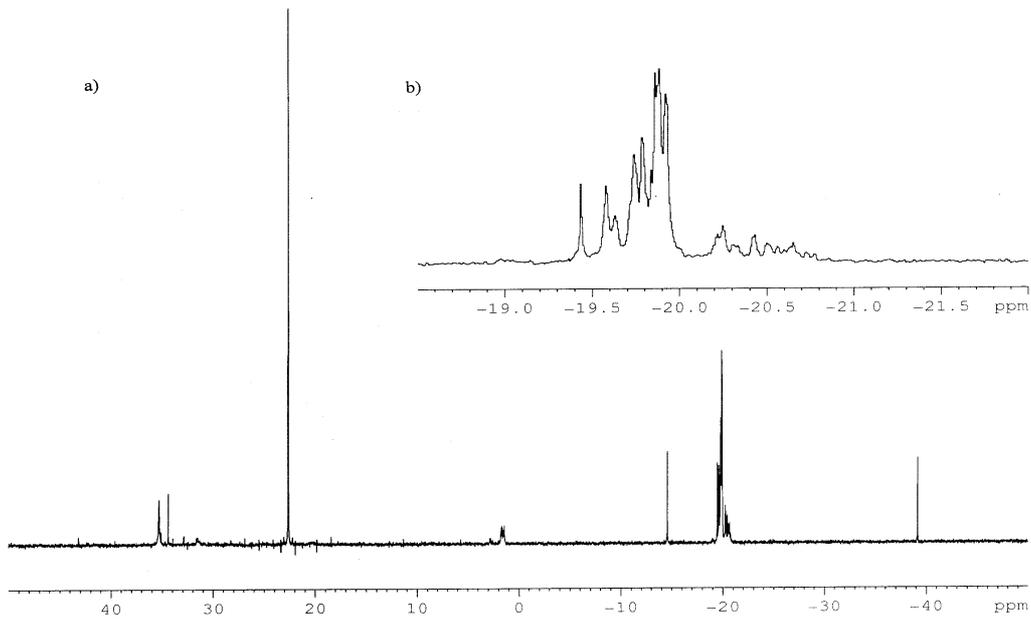


Figure 1: ^{31}P NMR spectra of PSMI a) from 50 to -50 ppm and b) from -18,5 to -22 ppm

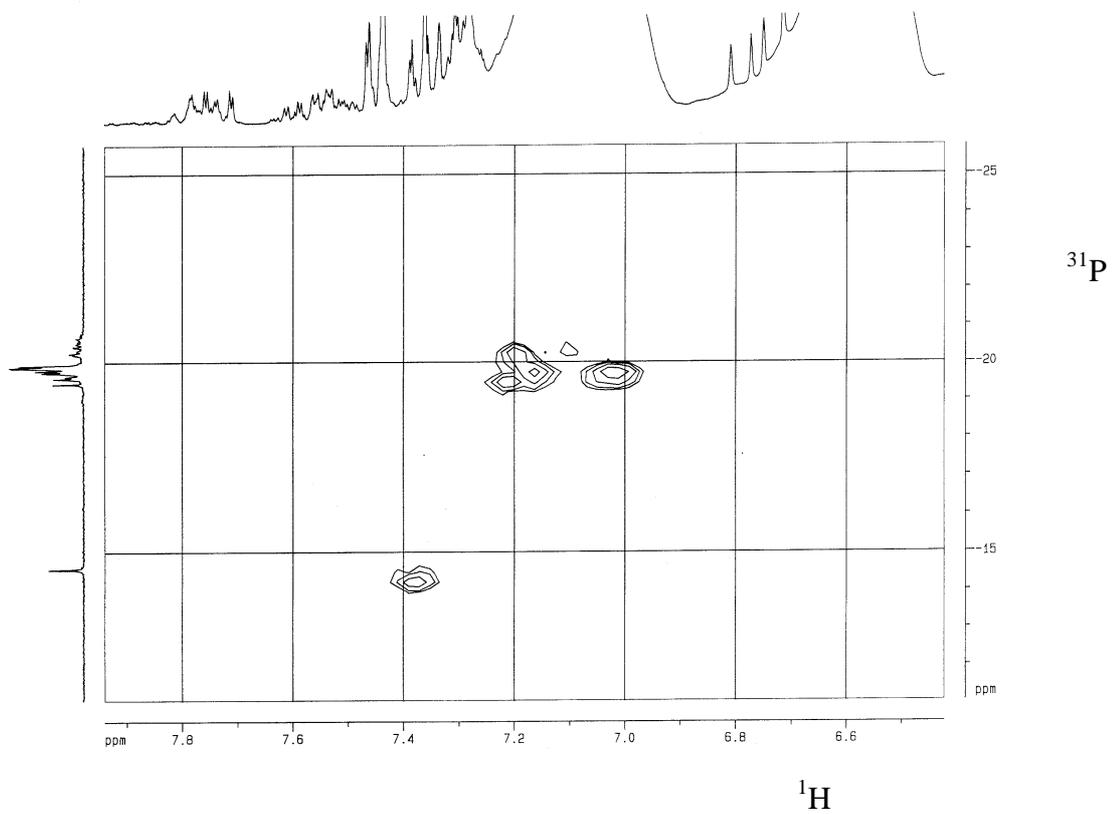


Figure 2: 2D HMBC NMR spectrum of polystyrene macroinitiator PSMI

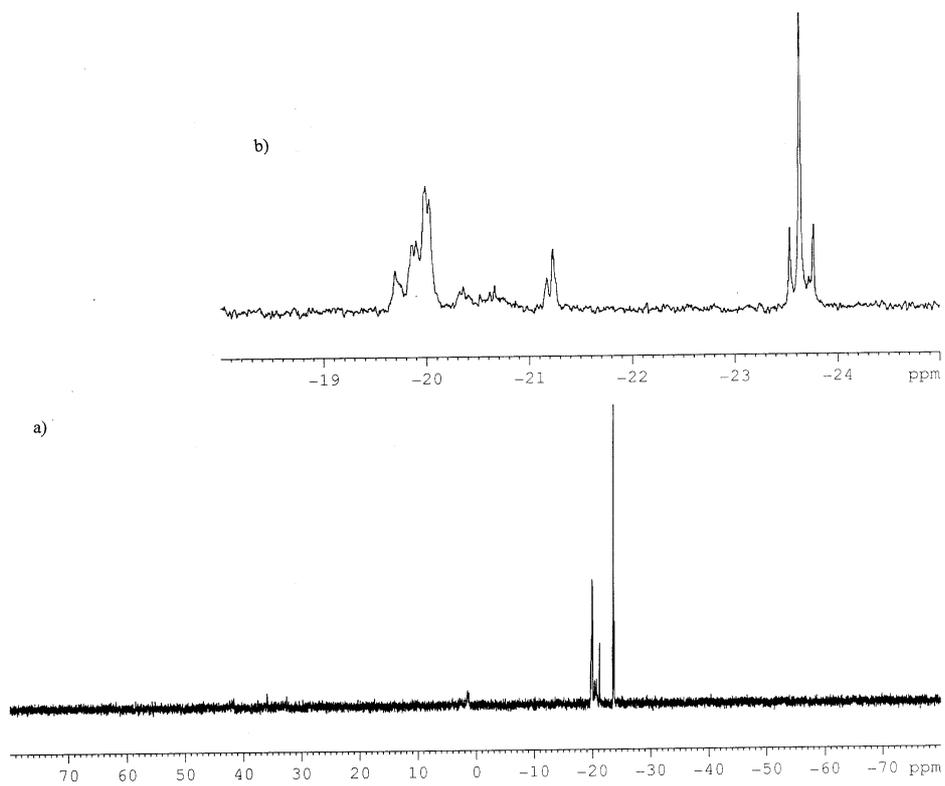


Figure 3: ^{31}P NMR spectra of block copolymer a) from 80 to -80 ppm and b) from -18 to -25 ppm

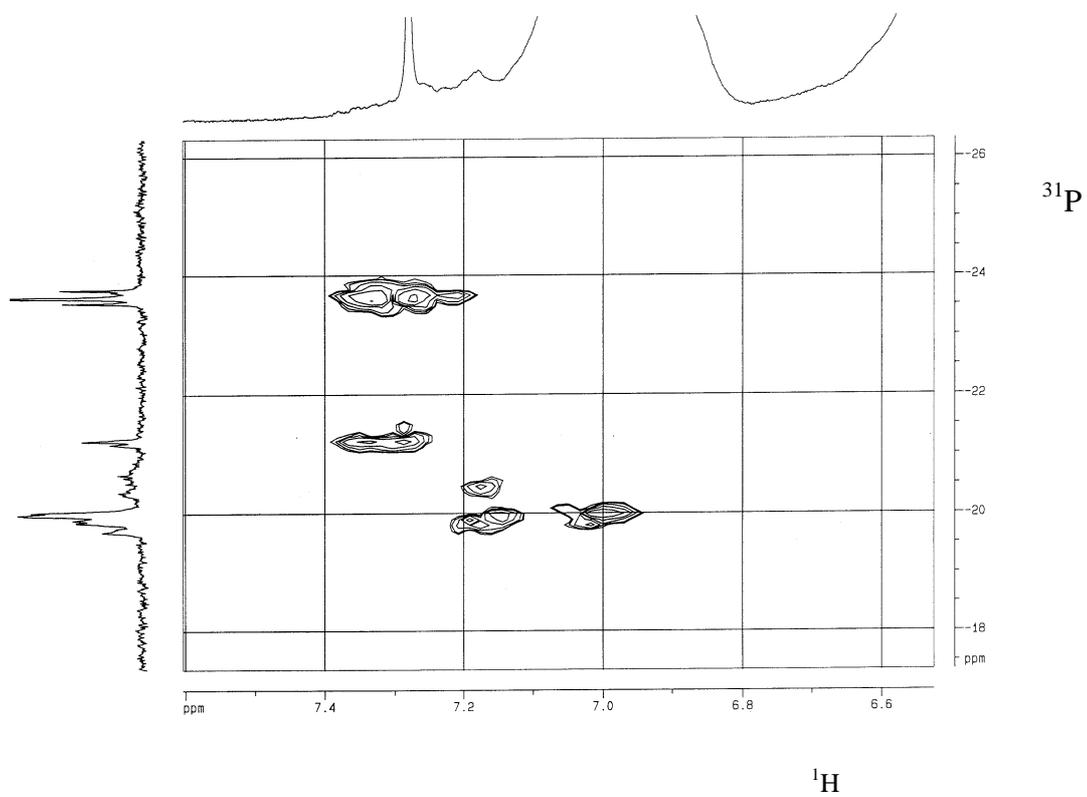
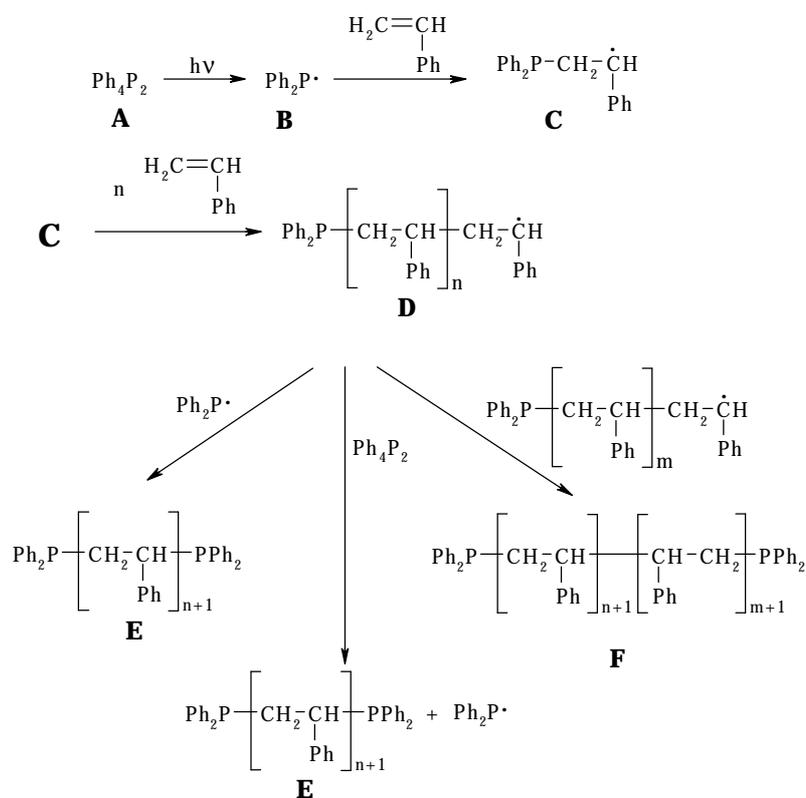


Figure 4: 2D HMBC NMR spectrum of block copolymer PS-PMMA

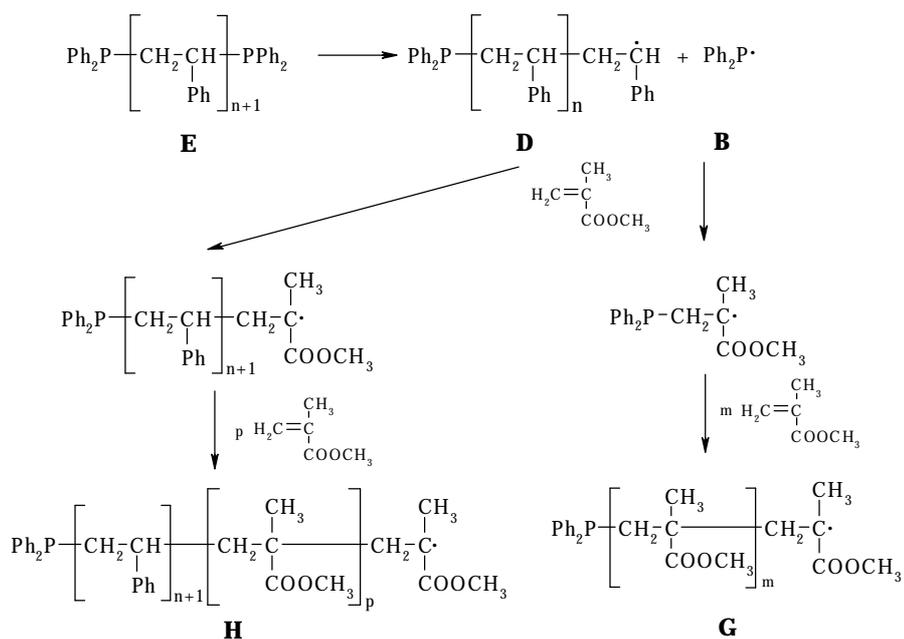
The peak at -14 ppm on phosphorus scale represents Ph_4P_2 which is an impurity in this case.

In ^{31}P spectrum of block copolymer PS/MMA (Figure 3) peaks close to -20 ppm belong to the polystyrene with (Ph_2P) end-groups in head and tail forms. Peaks at -23.6 ppm belong to the end group of polymethyl methacrylate in the tail form and peaks at -21.2 ppm belong to the end group in the head form of polymethyl methacrylate. The two dimensional ^{31}P - ^1H NMR spectrum (Figure 4) of the block copolymer has cross-peaks at 7.2 and 7.0 ppm on the proton scale representing tail and head bonding of end-groups to polystyrene. Peaks between 7.2 and 7.4 ppm on the proton scale represent tail and head bonding of end groups to polymethyl methacrylate.

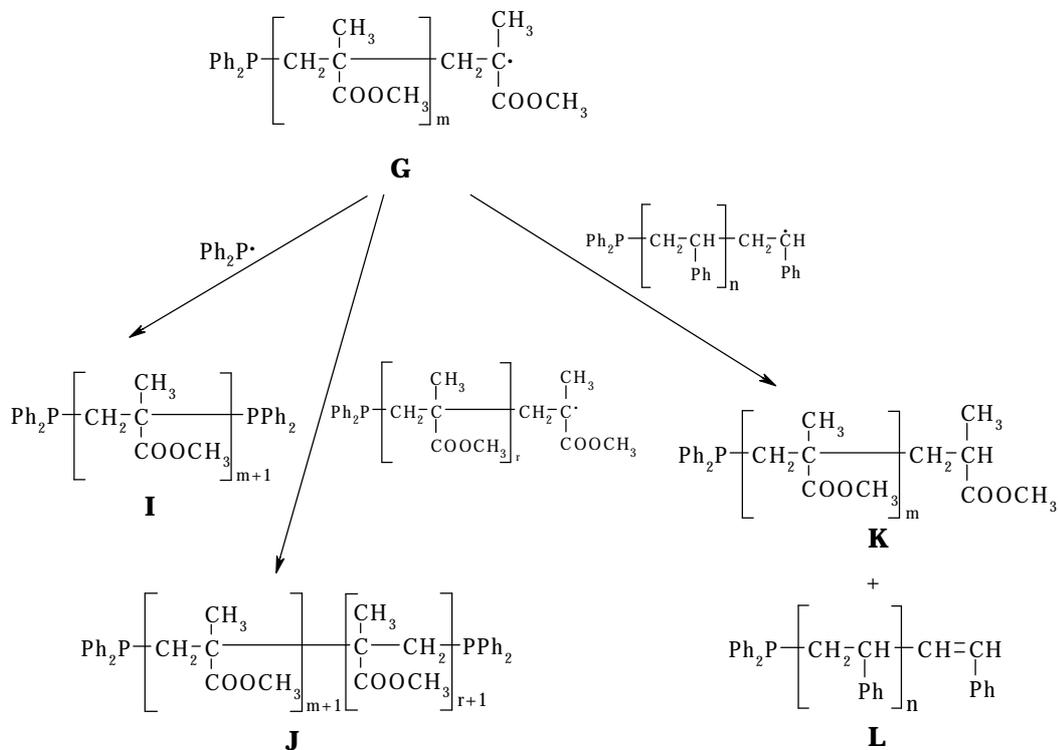
Reaction mechanism: Considering the results of all measurements, the following polymerization mechanisms were predicted [10]: Preparation of PSMI (Scheme 1); Initiator Ph_4P_2 (**A**) dissociates under the influence of UV light into two radicals $\text{Ph}_2\text{P}\cdot$, (**B**) and react with styrene to form styrene free-radicals (**C**), which start the propagation



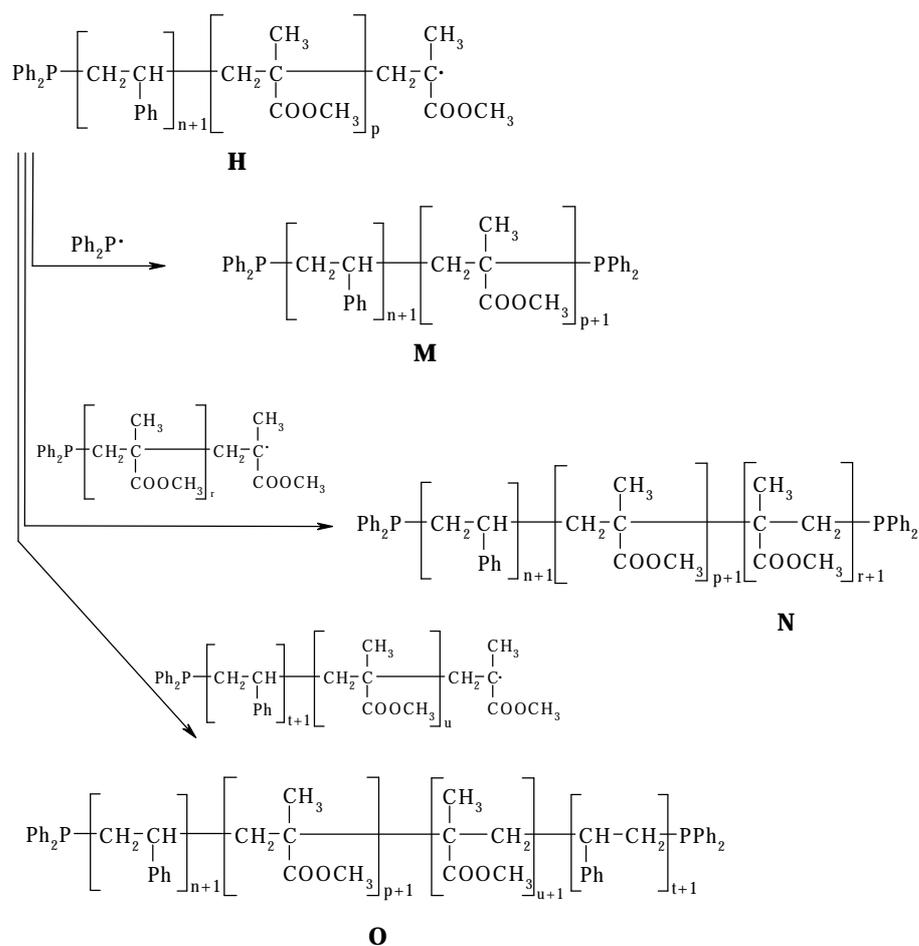
Scheme 1: Mechanism of the synthesis of polystyrene macroinitiator (PSMI)



Scheme 2: Mechanism of the copolymerization of polystyrene macroinitiator (PSMI) and methyl methacrylate (MMA)



Scheme 3a: Termination mechanism of a macroradical G



Scheme 3b: Termination mechanism of a macroradical H

of styrene monomer units. At the end of the polymerization the macroradical (**D**) terminates in three possible ways to form PSMI products (**E**) and (**F**) which can be stored in an inert atmosphere for later use. Synthesis of block copolymers (Scheme 2); Polystyrene macroinitiator (**E**) dissociates under the influence of UV light into two radicals which react with MMA to form intermediates: the polymethyl methacrylate free radical (**G**) and the polystyrene-polymethyl methacrylate free radical (**H**). Each of these two terminates in three possible ways. Intermediate (**G**) gives polymethyl methacrylate homopolymers (Scheme 3a) (**I**), (**J**), (**K**) and polystyrene homopolymers (**L**), whereas intermediate (**H**) terminates (Scheme 3b) into various polystyrene-polymethyl methacrylate block copolymers (**M**), (**N**) and (**O**).

CONCLUSION

The initiator tetraphenyl biphosphine (Ph_4P_2) is highly oxygen – sensitive. Consequently, it requires special reaction conditions. When exposed to UV light it decomposes into two radicals $\text{Ph}_2\text{P}\bullet$ which react with styrene to form styrene - free radicals capable of starting propagation. These radicals can terminate in various ways. The synthesized polymer with Ph_2P end groups acts as a macroinitiator in the second step of the polymerization in which block copolymers are formed. We found out that in the second step the pseudoliving mechanism is not predominant.

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POVZETEK

PS/PMMA blok kopolimere smo sintetizirali iz polistirenskih- (PS-) makroiniciatorjev z aktivnimi fosforjevimi aromatskimi končnimi skupinami z uporabo UV svetlobe. Proučevali smo vpliv valovne dolžine svetlobe in vpliv razmerja iniciator-monomer na stopnjo konverzije polimerizacije makroiniciatorja in blok-kopolimerizacije stirena in metilmetakrilata. Molska masa

blok kopolimerov narašča s polimerizacijskim časom. Za blok kopolimerizacijo stirena in metilmetakrilata s PS-makroinicijatorjem je primernejša svetloba z valovno dolžino 302 nm kot svetloba z valovno dolžino 366 nm. Makroinicijatorji razpadejo na primarni fosforjev radikal in makroradikal. Makromolekule terminirajo s primarnim radikalom, s kombinacijo dveh enakih ali različnih makroradikalov, kar smo opazovali z NMR spektroskopijo. Posamezne deleže homopolimerov in blok kopolimera v produktu smo določili z ekstrakcijo trdno-tekoče.