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# Nanofibres and Nanotubes in Radical Polymerisation

## Abstract

The course of styrene (S) polymerisation with the inclusion of SiC nanofibres (SiCNF) was compared with the course of reaction with singlewall carbon nanotubes (SWNT), whose radical activity has formerly been studied with respect to the polymerisation of another vinyl monomer – methyl methacrylate (MMA). The radical polymerisation of styrene in *N,N*-dimethylformamide (DMF) initiated by 4,4'-azobis(4-cyanopentanoic acid) (ACPA) at 333K in the presence of SiC nanofibres and SWNT was investigated by the dilatometric method. The principal difference in the chemical structure of the nanoparticles investigated is that the monomers influence their activity in the polymerisation. The SWNT act as low-effective inhibitors in the polymerisation of S and MMA but in an essentially different manner, whereas SiCNF have no impact on the process. The presence of carbonaceous nanoparticles in the processes investigated influences the thermal properties of polymerisation products differently.

**Key words:** nanofibres, carbon nanotubes, radical polymerisation.

## Introduction

Earlier investigations determined that various carbon forms: nanofibres [1 - 3], single- and multiwalls carbon nanotubes [4 - 8], fullerenes [4, 5, 9] and carbon black [7], graphite [7] or silicone carbide [4] exhibit different radical activity depending on the reaction medium. Vinyl monomers are often the model objects in scientific investigations, which supports the explanation of the interaction mechanism of various radical scavengers in both biological and technological applications [10, 11].

The research method, based on a polymerisation model, is a technique also allowing to distinguish the kind of deactivated radicals (primary or growing). The dilatometric technique applied to kinetic measurements [12] is simultaneously the source of polymer obtained under precisely defined conditions – in an oxygen-free medium with known degree of conversion. This allows to complete kinetic data with examinations of polymer properties.

Previous studies [10] concerned the influence of carbonaceous substances on methyl methacrylate and acrylonitrile polymerisations. This work also concerns testing the influence of carbonaceous nanoparticles on the polymerisation of another vinyl monomer – styrene. Such

a class of monomers is utilised for fiber-forming polymers.

## Experimental part

### Materials

The following monomers: styrene (S), methyl methacrylate (MMA) and a solvent: *N,N*-dimethylformamide (DMF) were purified by standard methods. Azoinitiator 4,4'-azobis-4-cyanopentanoic acid (ACPA) (Du Pont) was used without further purification. SiC nanofibres (with a diameter of 20 - 100 nm and length of up to several tens of microns), synthesised at the Chemical Department of Warsaw University [2], and single wall carbon nanotubes containing 30% of appropriate SWNT (with a diameter of 0.7 - 1.2 nm and length 2 - 20  $\mu\text{m}$ ) from MER Corp. USA were used as received.

### Measurements

Polymerisation was carried out in a nitrogen atmosphere at 60 °C in dilatometers (glass reactors with a capacity of 35 cm<sup>3</sup>) with a capillary tube. Before the polymerisation carbonaceous substances in various amounts were sonicated in DMF for 15 min and added to an initiator–monomer mixture prepared separately. Constant concentrations of the monomer and initiator were established on the basis of our earlier investigations [5 - 7].

Monomer conversion during the polymerisation was achieved using the dilatometric method according to the procedure described precisely in [12]. Utilising the volume contraction phenomena during the reaction, the change in the volume of the reaction mixture was ob-

served, and the degree of conversion  $p$  was determined from equation:

$$p = \frac{\Delta V_t^T}{V_M^T \cdot L^T} \quad (1)$$

where  $\Delta V_t^T$  is the change in the reaction mixture volume after time  $t$  in min,  $V_M^T$  is the volume in cm<sup>3</sup> of monomer in the reaction mixture at reaction temperature  $T$ , and  $L^T$  is the relative change in the specific volume of the reaction mixture at a monomer conversion of 100%.

Subsequently, plotting the logarithmic dependence of conversion  $p$  for time  $t$ :  $\ln[1/(1-p)] = f(t)$ , the tangent of the slope of the straight line allows the evaluation of the polymerisation rate  $R_p$  in mol·dm<sup>-3</sup>·min<sup>-1</sup>, taking into account the monomer concentration  $[M]$  in mol·dm<sup>-3</sup>:

$$R_p = \frac{d}{dt} \ln \frac{1}{1-p} \cdot [M] \quad (2)$$

The overall rate constant was calculated from the general expression for the rate of polymerisation, for both the polymerisation without carbonaceous nanoparticles (the model polymerisation) and with their inclusion according to equation [5, 7]:

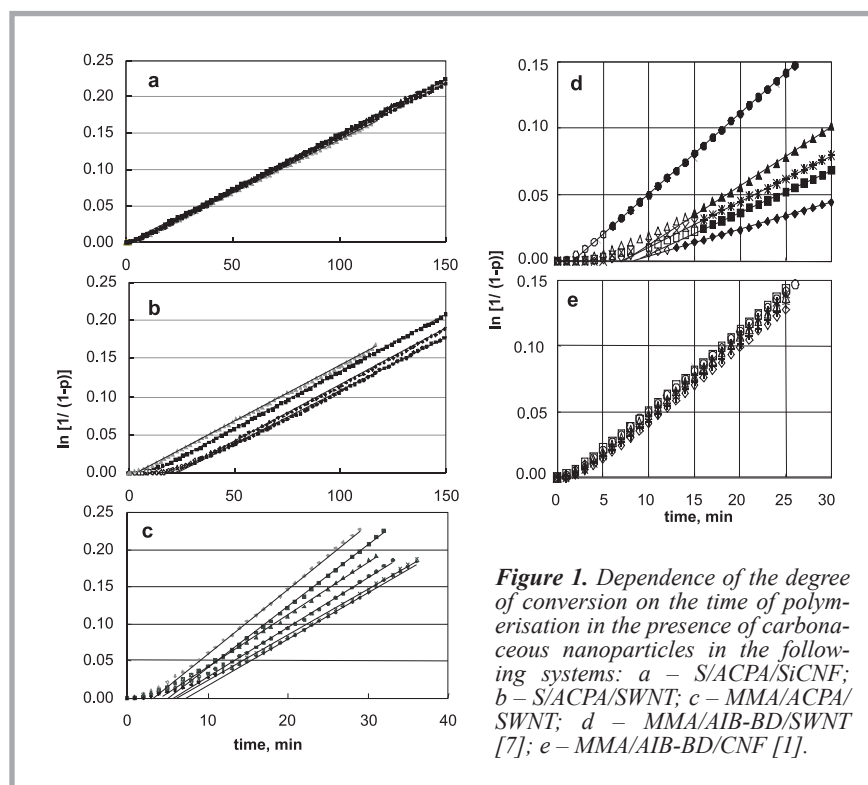
$$R_{p,x} = K_X \cdot [M] \cdot [I]^{0.5} \quad (3)$$

Variable parameter  $K_X$  characterises the polymerisation rate in the presence of an inhibitor; it takes the value of the overall rate constant of the polymerisation in the absence of an inhibitor.

The polymers were isolated by precipitation into a non-solvent and then purified from the residual unreacted carbonaceous nanoparticles by repeated dissolution in

**Table 1.** Kinetic parameters of radical polymerisation in the presence of carbonaceous nanoparticles.

	[X], g·dm <sup>-3</sup>	R <sub>p,X</sub> , mol·dm <sup>-3</sup> ·min <sup>-1</sup>	K <sub>X</sub> , dm <sup>1.5</sup> mol <sup>0.5</sup> ·min <sup>-1</sup>	t <sub>i</sub> , min
<b>S/ACPA/SiCNF/DMF system; [S]=7.5mol·dm<sup>-3</sup>, [ACPA]=0.06mol·dm<sup>-3</sup></b>				
S0	0	0.01043	0.00611	4
S1	1.34	0.01053	0.00638	4
S2	2.74	0.01082	0.00646	5
S3	4.42	0.01051	0.00643	2
<b>S/ACPA/SWNT/DMF system; [S]=7.5mol·dm<sup>-3</sup>, [ACPA]=0.06mol·dm<sup>-3</sup></b>				
S0	0	0.01043	0.00611	4
S4	1.32	0.01051	0.00624	11
S5	2.71	0.01002	0.00592	24
S6	4.52	0.01064	0.00626	23
<b>MMA/ACPA/SWNT/DMF system; [MMA]=6mol·dm<sup>-3</sup>, [ACPA]=0.06mol·dm<sup>-3</sup></b>				
M0	0	0.04950	0.03656	3
M1	1.35	0.04760	0.03554	6
M2	3.29	0.04146	0.03112	5
M3	4.68	0.03897	0.02901	6
M4	6.98	0.03700	0.02798	8
M5	9.15	0.03628	0.02766	8



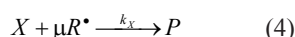
**Figure 1.** Dependence of the degree of conversion on the time of polymerisation in the presence of carbonaceous nanoparticles in the following systems: a – S/ACPA/SiCNF; b – S/ACPA/SWNT; c – MMA/ACPA/SWNT; d – MMA/AIB-BD/SWNT [7]; e – MMA/AIB-BD/CNF [1].

the solvent, filtration and precipitation. The final polymer samples were dried under reduced pressure and examined by IR spectroscopy and thermal analysis (DSC or DTA).

## Results and discussion

The mechanism of radical polymerisation, in the simplest case, consists of elementary reactions: initiator decomposition, initiation, propagation and termination. If polymerisation occurs in the pres-

ence of a substance which is additionally introduced to the reaction medium and chemically active towards radicals ( $R^\bullet$ ), it can be schematically expressed in the form of a general reaction [5]:



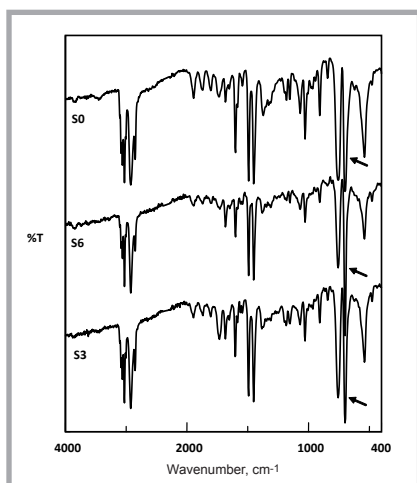
where  $X$  denotes the additional reagent,  $R^\bullet$  – any kind of radical,  $k_X$  – reaction rate constant,  $\mu$  – stoichiometric factor that corresponds to the number of radicals deactivated by one molecule of the additional reagent,  $P$  – unreactive product of the reaction.

If the substance can quantitatively scavenge the initiating radicals, further propagation cannot occur during the time of its exhaustion. After that the reaction proceeds as rapidly as polymerisation in its absence, such a compound is referred to as the inhibitor. The substance that in low concentration effectively suppresses the overall rate of polymerisation without an induction period ( $t_i$ ) is known as a retarder. The distinction between retarders and inhibitors is not always clear [13].

The same substance, e.g. fullerenes, depending on the reaction medium (with a change in the kind of monomer) can be an inhibitor or retarder, which we observed in earlier investigations by the model reaction method [5, 7, 10], which consists in the polymerisation of the model monomer with the substance tested, determination of kinetic parameters of the reaction and referring them to the polymerisation without its inclusion. Results of the polymerisation systems tested in this work are collected in **Table 1** and **Figure 1**, in which they are additionally compared with the systems studied earlier [1, 7].

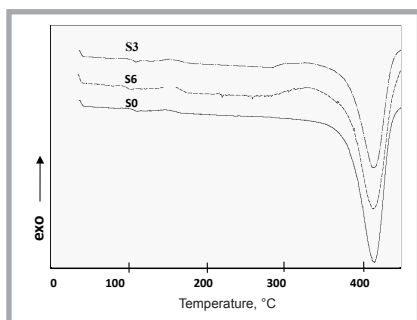
Styrene polymerisation with carbon nanotubes (**Figure 1.b** and **Table 1**) is characterised by an induction period, which lengthens with an increase in the amount of SWNT in the reaction mixture, whereas the overall rate of polymerisation does not change. The different influence of SWNT is observed in the methyl methacrylate polymerisation (**Figure 1.c**), that is: the process rate decreases with an increase in SWNT concentration in the reaction mixture, and the induction time changes in a small range. Thus the influence of carbon nanoparticles in the form of SWNT in the course of the polymerisation of S and MMA is visible and different. The occurrence of the induction time in styrene polymerisation is connected with the fact that carbon nanotubes are more reactive to primary radicals than the monomer. Styrene, as an electron donor, is not a rival for nanotubes in the reaction with radicals, unlike methyl methacrylate, which is an electron acceptor.

The presence of another kind of carbonaceous material – SiC in the form of nanofibres – in styrene polymerisation under the same conditions does not cause any changes in its course, i.e. the polymerisation rate does not change, and there is no induction time (**Figure 1.a**).

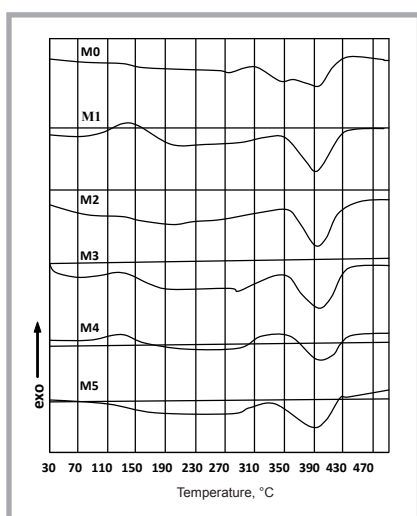


**Figure 2.** IR spectra of polystyrenes: S0 – PS, S3 – PS/SiCNF, S6 – PS/SWNT

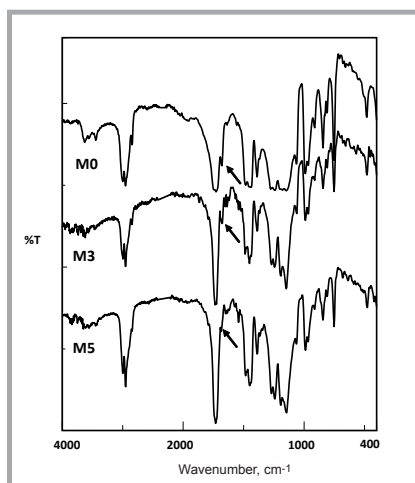
Similarly our previous investigations have shown that the presence of carbon nanofibres (CNF) does not influence MMA polymerisation initiated by 2,2'-azobis(2-methyl-4-hydroxybutyl propionate) (AIB-BD) (**Figure 1.e**) [1], whereas the SWNT in this reaction system cause a decrease in the polymerisa-



**Figure 4.** DSC thermograms of polystyrenes: S0 – PS, S3 – PS/SiCNF, S6 – PS/SWNT.



**Figure 5.** DTA thermograms of poly(methyl methacrylates).



**Figure 3.** IR spectra of poly(methyl methacrylates).

tion rate with an increase in the SWNT concentration in the reaction mixture (**Figure 1.d**) [7], as in polymerisation initiated by ACPA.

The examinations of the polymerisation products confirm the kinetic observations. On the basis of both the IR spectroscopy of polymers (**Figures 2, 3**) and their thermal analysis (**Figures 4, 5**), the influence of SWNT on the properties of polystyrenes and poly(methyl methacrylates) is visible, while in the case of polymers with SiC nanofibres no changes are observed.

The carbon occurring in various forms: fullerenes, single- and multiwalled carbon nanotubes, carbon nanofibres or silicone carbide is characterised by different chemical activity towards alkyl radicals in the polymerisation. While fullerenes, C<sub>60</sub> show high reactivity; SWNT have less and the silicone carbide does not show any activity regardless of its physical form (powder or nanofibres) and the kind of monomer (electrophilic or electron-donating).

## Conclusions

The method presented with the application of the model polymerisation allows to evaluate the influence of the presence of carbonaceous nanoparticles on the course of radical polymerisation and the properties of reaction products.

SWNT distinctly change the course of polymerisation of vinyl monomers and, depending on their kind, SWNT reactivity occurs as an inhibitor in S polymerisation and a retarder in MMA polymerisation.

SiC nanofibres do not show radical activity, similar to carbon nanofibres (CNF) in MMA polymerisation systems.

The thermal analysis of polystyrenes indicates that carbon nanotubes (SWNT) shift the onset of degradation to a lower temperature, possibly due to the higher thermal conductivity of polymer with SWNT.

The thermal investigations of poly(methyl methacrylates) show that SWNT change the mechanism of depolymerisation of model polymer from a two-stage to a one-stage, which probably results from the lower content of terminal double bonds in the polymer.

## Acknowledgment

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