

# 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