

Synthesis and Surface Tension Properties of Polyethyleneimine-Polyethylene Oxide Block Copolymers

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This paper describes the synthesis, surface tension and dispersancy properties of block copolymer nonionic surfactants comprised of polyethyleneimine (PEI) and polyethylene oxide (PEO) blocks of selected lengths. These block copolymers were prepared by a three-step synthetic sequence. Firstly, PEO glycol was converted to its dimethanesulphonylester (dimesyl) derivative by reacting with methanesulphonyl chloride. Then a tri-block polymer was prepared by the ring-opening polymerization of 2-methyl-2-oxazoline (MeOZO) with the dimesyl PEO derivative. Lastly, linear PEI blocks were obtained by subsequent hydrolysis and purification. ¹H NMR spectra confirmed the structures of the intermediate, final products and their purities (>99%). The utility of these block copolymers is described in terms of their surface tension and clay dispersancy measurements as a function of copolymer chain and block length.

Keywords block copolymer, polyethylene oxide, polyethyleneimine, surface tension, clay dispersancy

Introduction

In recent years there have been increasing activities in block copolymer synthesis and characterization. Many studies have shown that block copolymers form micelles of close association upon dissolution into a selective solvent, which acts thermodynamically as a good solvent for one block and a poor solvent for the other block.¹ The importance of these synthetic activities has been emphasized by block copolymer micelles, which have been demonstrated as potential drug carriers,^{2,3} and other investigations have revealed their excellent utility in cancer chemo-therapy.⁴

Block copolymers that are comprised solely of water-soluble block units are best represented by poly(ethyleneoxide)-poly(propyleneoxide)-poly(ethyleneoxide) tri-block polymers (PEO-PPO-PEO). These commercially available materials with important properties are very useful from a technological point of view, such as steric stabilizers for latex particles and as dye or pigment vehicles in printing technologies⁵ as well as drug delivery systems.⁶

This report describes the preparation of block copolymer nonionic surfactants comprised of polyethyleneimine and

polyethylene oxide blocks (PEO-PEI-PEO) and the utility of these copolymers in terms of surface tension and clay dispersancy as a function of copolymer chain and block length. The preparation of these materials is based on our investigations on the ring opening polymerization of 2-methyl-2-oxazoline (MeOZO) by terminally di-functionized alkyl sulphonate initiators to produce poly(*N*-acylethylenimine) segments. With this "living" ring-opening polymerization,⁷ a careful control of the number of amide groups, and subsequently the number of amine units in the final tri-block copolymer after hydrolysis and purification may be obtained. This careful control gives a better understanding of the effect of PEI block size on the surface tension and clay dispersancy properties of the final ABA tri-block copolymers.

Experimental

Materials

2-Methyl-2-oxazoline (MeOZO) was supplied from Aldrich Chemical Co. and purified by repeated distillations over KOH pellets in an inert atmosphere. Methanesulfonyl chloride was a commercial reagent (Kanto Chemical Co.) and was used as received. Acetonitrile (Kanto Chemical Co.) was dried over CaH₂ and distilled. Triethylamine (Kanto Chemical Co.) and dehydrated benzene (Kanto Chemical Co.) were dried over KOH and distilled in an inert atmosphere prior to use. Commercial PEO samples (nominal molecular weights of 600, 1000, 2000, 4000 and 20000 daltons) were purchased from Wako Pure Chemical Industries Ltd. and used as received.

Preparation of methanesulphonic acid diester of PEO (Ms-PEO)

As a typical example, a solution of methanesulfonyl chloride (17.2 g, 0.15 mol) diluted in 60 mL of anhydrous benzene was dripped over a period of 1 h to a stirred solution

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of PEO 1000 (50.0 g, 0.05 mol) and triethylamine (15.1 g, 0.15 mol) in 180 mL of anhydrous benzene under ice water cooling. The reaction was continued for 22 h at room temperature. During the reaction, a yellow precipitation gradually was formed. To ensure a complete reaction, the mixture was warmed for another 2 h at 40 °C. The mixture was suction-filtered and treated with 200 mL of saturation NaHCO₃ solution. The mixture was extracted with 100 mL of benzene, and the benzene layer was dried over Na₂SO₄ and filtered, giving a pale yellow liquid after solvent removal *in vacuo*. Typical yields of all materials were approximately 98%.

Preparation of block copolymers polyethyleneoxide-*b*-polyacetyl ethyleneimine (PEO-*b*-PACeI)

Block copolymerizations were carried out in dried, distilled acetonitrile. As a typical example, MsPEO1000 (17.3 g, 0.015 mol), triethylamine (6.06 g, 0.06 mol), 60 mL of acetonitrile, and MeOZO (51 g, 0.6 mol) were added sequentially under N₂ atmosphere to a 200-mL tube with a magnetic stirrer. The tube was sealed and placed into an 80 °C oil bath. Heating and stirring were continued for 24 h. After cooling to room temperature, the mixture was treated with 20 mL of aqueous Na₂CO₃ (10% wt) and stirred for another 2 h. Solids were removed by filtration and the solution was dried (Na₂SO₄) and evaporated under vacuum to remove acetonitrile and any residual water. The block copolymer was purified further by reprecipitation from warm chloroform into hexane (non-solvent). The pale yellow solid material was dried *in vacuo*. The yield was 99%. Yields of other copolymers using the same technique ranged from 96%—99%.

Alkaline hydrolysis of PEO-*b*-PACeI to PEO-*b*-PEI

As a typical example, in a 500-mL flask, PEO(2000)-*b*-PACeI(5 × 2) (30 g, 0.01 mol), NaOH (6 g, 0.15 mol) and 100 mL of H₂O were added. The hydrolysis was conducted at 100 °C with stirring. After a 24—96 h reaction period, the mixture was cooled to room temperature and water was removed *in vacuo* to give a white solid product.

Purification of final product (PEO-*b*-PEI)

The following purification method was adopted to completely remove sodium acetate from the hydrolysis mixture. As an example, product (32 g) mixture was dispersed in 100 mL of hot chloroform in a 50 °C oil bath, stirring for 1—2 h. Solid and liquid phases were separated by centrifugation. The liquid portion was further filtered through a column packed with Celite. Chloroform was removed *in vacuo* and the solid obtained was further dried at high vacuum at 60 °C. The percent recovery of purification is 96%. Yields of other copolymers using the same technique ranged from 95%—97%.

Analytical methods

¹H NMR spectra were recorded at 27 °C on a Bruker ARX-400 spectrometer (Bruker, Karlsruhe, Germany) in

CDCl₃ with tetramethylsilane (TMS) as an internal standard.

Surface tension measurements

Surface tension was measured using a K12 tensiometer (Kruss GmbH, Hamburg, Germany). The measuring unit consisted of a force-measuring system, a temperature sensor, a thermostatic jacket with a built-in magnetic stirrer and a platform drive system (to raise and lower the sample automatically and set its position). The surface tension itself was measured by the plate method of Wilhelmy,⁸ using a clean, rectangular platinum plate attached to the force sensor (flame-dried before each measurement). The sample surface was raised until it came into contact with the plate edge, with force on the plate rising immediately upon contact with the liquid surface. The instrument then recorded the surface position to make sure that the bottom edge of the plate is maintained tangent to the surface. Under these conditions, force is directly proportional to surface tension. The equipment was calibrated with double-distilled water. Measurements were taken at atmospheric pressure and at least 10 replicates were performed to ensure reproducibility. These results were then averaged, and standard deviation values were found to be within 0.08 mN/m.

Clay dispersancy studies

Dispersancy tests were conducted to evaluate clay (inorganic particulate) dispersancy of these materials as potential laundry detergent builders by measuring transmittance of clay solution (containing copolymer samples) using a photo electrode (Mettler photo electrode DP550, Mettler-Toledo AG, Schwerzenbach, Switzerland). Lower transmittance indicates better dispersancy.⁹ Clay dispersions used are the combination of buffer solution, clay, and hardness stock solution. The buffer solution consisted of glycine (0.06 g/mL), NaCl (0.05 g/mL) and 1 mol/L NaOH (0.1 mL/mL). A 1000 gpg hardness stock solution consisted of CaCl₂·2H₂O (0.0188 g/mL) and MgCl₂·6H₂O (0.0086 g/mL). The concentration of copolymer sample in each case was 5 × 10⁻⁵ throughout all measurements. Measurements were made at pH 8.8, in presence of three different hardness levels, 3 gpg, 6 gpg and 9 gpg.

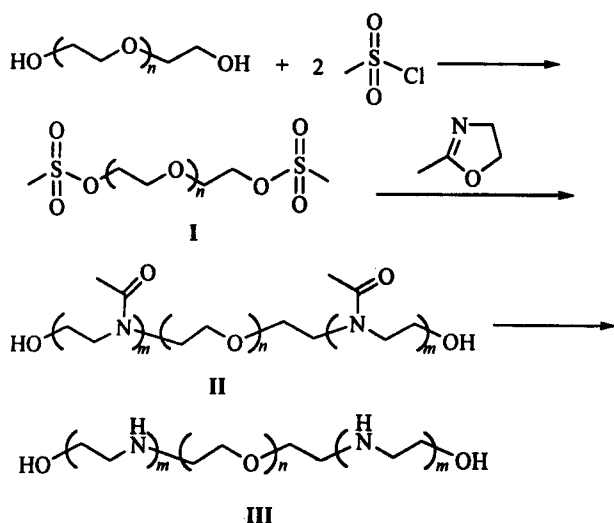
The electric potential (transmittance) value was initially adjusted on the instrument (Mettler titrator DL25, Mettler-Toledo AG, Schwerzenbach, Switzerland) to 1000 mV with deionized water. The photo-electrode was dipped into the test tube containing the dispersancy test solution which had been prepared 20 h earlier, and a timer started. A stable transmittance (in mV) was recorded 2 min after introduction of the photo-electrode. Every sample was measured at least twice and the results were then averaged, and standard deviation values were found to be within 1 mV. During the analysis a blank sample was measured between each solution measurement to ensure minimal drift.

Results and discussion

Material synthesis

The synthesis of PEO-PEI copolymers was divided into three steps. The first step was the preparation of methanesulphonic acid diester (dimesyl) of PEO (I) by reaction with methanesulphonyl chloride. The second step was the preparation of block copolymer. Dimesyl PEO (MsPEO) was used to initiate a ring-opening polymerization of 2-methyl-2-oxazoline MeOZO to obtain an ABA tri-block copolymer (PEO-*b*-PACeI) (II). Finally the resulting PEO-*b*-PACeI was subjected to alkaline hydrolysis, in which the blocks of poly(*N*-acetyleneimine) were converted into linear polyethyleneimine groups (III) (Scheme 1).

Scheme 1



Preparation of dimesyl PEO

PEO's of three different M_w values were converted to their dimesyl derivatives by reaction with methanesulphonyl chloride. They are No. 600 ($M_w = 600$), No. 1000 ($M_w = 1000$) and No. 2000 ($M_w = 2000$). Typical yields of all materials were approximately 98%.

In the ¹H NMR spectrum of MsPEO1000 after reaction and purification, a signal due to methyl proton was observed at δ 3.05, as well as a peak corresponding to methylene protons adjacent to the sulphonic ester group at δ 4.35 (Fig. 1). The data confirm that the methane sulphonyl-terminated structure of MsPEO. Also, the NMR data show that the purity of MsPEO is quite high.

Polymerization of MeOZO

PEO which was terminally substituted with mesylate functionalities was used to initiate a ring-opening polymerization of MeOZO giving an ABA tri-block copolymer. The

block copolymerizations were carried out in acetonitrile at 80 °C, and required reaction time at least 72 h. Pale yellow solid copolymers were obtained almost quantitatively. Using this procedure three PEO starting materials each provided four types of PEO-*b*-PACeI copolymers ranging from average blocks units of $n = 3$ to $n = 20$.

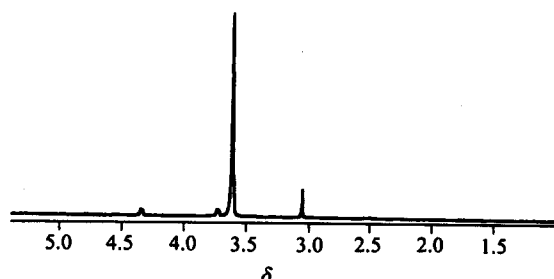


Fig. 1 ¹H NMR spectrum of MsPEO (I).

The optimum temperature for ring-opening polymerization was 80 °C and the optimum reaction time was 72 h to ensure complete reaction. These reaction conditions favor the electrophilic addition of the methane sulphonyl moieties to the nitrogen center of MeOZO. The resulting oxazolium salts were added to the nucleophilic MeOZO, thus providing the ring-opening polymerization. The nucleophilicities of the oxazolium salts are lower than that of MeOZO itself,¹⁰ and the relative nucleophilicities of the oxazolium sites are lowered even further in the presence of aprotic amines.¹¹

Two solvents were employed to precipitate the block copolymer. We found hexane to be the best non-solvent. Thus, the block copolymer was isolated by decantation and purified further by reprecipitation from a small volume of chloroform (solvent) into a large volume of hexane (non-solvent). The pale yellow solid copolymers were dried *in vacuo* before characterization.

The ¹H NMR spectrum of PEO-*b*-PACeI shows a sharp singlet at δ 3.65 (due to PEO block) and two broad peaks at δ 3.4–3.6 (CH₂NCH₂) and at δ 2.0–2.25 [C(O)CH₃] (due to *N*-acetyl) (Fig. 2). The data supported PEO-*b*-PACeI as a tri-block copolymer of PACeI-PEO-PACeI. Comparing of the integrations of the PEO block and the clearly resolved *N*-acetyl signal allows to accurately determine the average block size of poly(*N*-acetyl ethyleneimine) blocks.

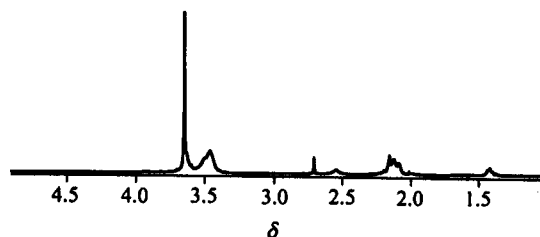


Fig. 2 ¹H NMR spectrum of tri-block copolymer of PACeI-PEO-PACeI (II).

Hydrolysis

PEO-*b*-PAAcEI materials were subjected to alkaline hydrolysis, in which the blocks of poly(*N*-acyliminoethylene) were converted into a linear polyethyleneimine block. The reaction was carried out in aqueous alkaline solution at 100 °C for 24 h. The resulting hydrolysis product, PEI-*b*-PEO-*b*-PEI, was obtained in 92% yield. The degree of hydrolysis was determined from the integral ratio of the signal of *N*-acetyl group (δ 2.1, s) of ^1H NMR spectrum to be 99%.

In the hydrolysis process, aqueous NaOH is used as the solvent and reaction agent. For successful hydrolysis the molar ratio between PAAcEI unit and NaOH is 1 to 1.5 at a minimum. Another key point for hydrolysis is that the different PEO blocks require the different reaction time for successful hydrolysis. For the copolymer of PEO(600)-*b*-PAAcEI there were no problems of solubility since it has a lower molecular weight. However, the same hydrolysis conditions could not be extended to PEO(2000)-*b*-PAAcEI.

With a reaction time of 24 h, the degree of hydrolysis for PEO(600)-*b*-PAAcEI block copolymer is nearly quantitative. For PEO(1000)-*b*-PAAcEI block copolymer, it is 30% but for PEO(2000)-*b*-PAAcEI there is still 25% unreacted PEO2000-PAAcEI by comparison of the signal of *N*-acetyl group (δ 2.1, s) in the ^1H NMR spectrum (Fig. 3). It required a reaction time of 96 h to complete the hydrolysis of PEO(2000) block copolymers. Therefore, by extending the time allowed for reaction, a successful PEO(2000)-*b*-PAAcEI hydrolysis in aqueous NaOH was achieved.

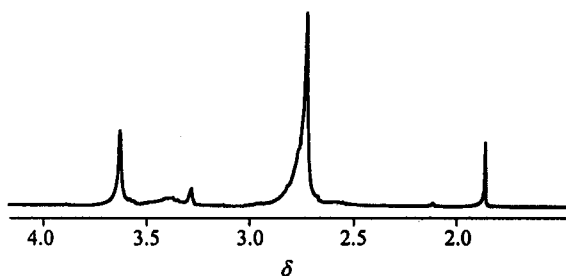


Fig. 3 ^1H NMR spectrum of PEO-PEI block copolymers.

Purification of the final product

Much of the literatures concerning PEO-PEI block copolymers have not dealt specifically with the purification of final product,¹⁰ but the existence of the hydrolysis by-products will influence the physical-chemical measurement results.¹² From Fig. 4(a), a significant amount of NaOAc, the reaction by-product, can be seen (δ 1.88). Therefore, an effective method for purification of the final product was undertaken.

Centrifugation followed by Celite filtration was chosen to remove the solid phase impurity (NaOAc). After an initial ultracentrifugal separation of a chloroform solution of the mixture, an open column packed with cotton and Celite was used for further filtration. Solvent was removed *in vacuo*. The ob-

tained yellow product was further vacuum oven dried.

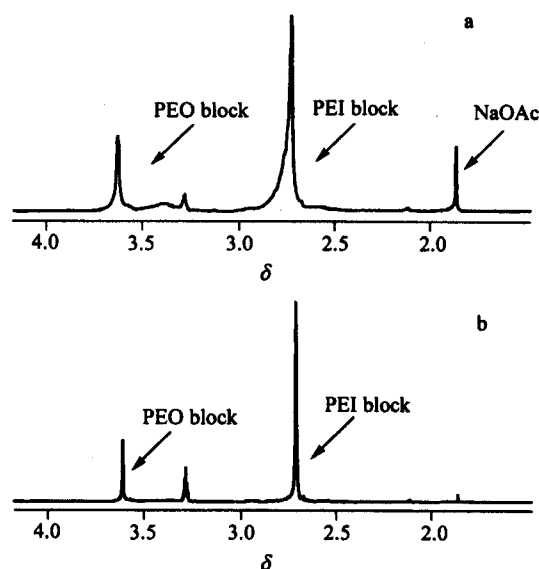


Fig. 4 ^1H NMR spectra of PEO(600)-*b*-PEI(20 \times 2) block copolymer. (a) Before purification; (b) after purification.

The ^1H NMR spectrum of PEO-*b*-PEI materials shows sharp signals due to the PEO (δ 3.65, s) and PEI (δ 2.75, s) blocks. The signal of *N*-acetyl group (δ 2.1, s) was not observed, indicating complete hydrolysis. However, a signal (δ 1.88, s) indicated the presence of NaOAc, the reaction by-product before purification. The above data confirm that the final product is PEO-*b*-PEI block copolymer and that hydrolysis is complete. From the spectra, it can be seen that the purification procedure is effective.

Surfactant properties

The surface tension properties of PEO and PEO-PEI derivatives have been investigated with respect to their molecular weights and the degree of amine substitution.¹³ However, the PEI materials studied were randomly branched and of relatively high molecular weight. The studies of the current report show that over the molecular weight range of 600 to 20000 there is essentially no change of surface tension properties for PEO itself (1% solution), although a separate study has shown a tendency to lower surface tension values with much higher PEO molecular weights.¹⁴ The addition of PEI units in an ABA block copolymer architecture gives a significant lowering of surface tension properties when compared to PEO itself, as is demonstrated in Fig. 5. The surface tension values for all PEO starting materials from M_w 600 to M_w 20000 are approximately 59 mN/m (0.5% and higher solutions). At low concentrations (0.01%) the introduction of PEI units seems to elevate the surface tension, at most to approximately 18% greater than that of PEO itself. At higher concentrations (0.1% and greater) the introduction of even a short PEI block into the polymer chain lowers

the surface tension properties of the aqueous solutions of these materials. The presence of PEI blocks serves to lower the surface tension and the gradual increase of PEI block lengths lowers the surface tension further. Increasing the concentration of the copolymers from 0 to 0.5% does lower the observed surface tension. Beginning at concentrations of from 0.4% to 0.6% (dependent upon PEO-PEI copolymer architecture) surface tension values remain constant. At concentrations of 0.6% and greater, all materials show values within a relatively narrow range. This twin action of lowering surface tension and having a minimal concentration effect is observed in all three PEO series examined here (PEO-600, PEO-1000 and PEO-2000) and has been observed in other PEI systems as well.¹⁵ This amine substitution effect is also demonstrated in the broad range of other alkylamine-substituted polyoxyethylene materials where all alkylamine-substituted PEO's have very similar surface tension properties regardless of amine content.¹³

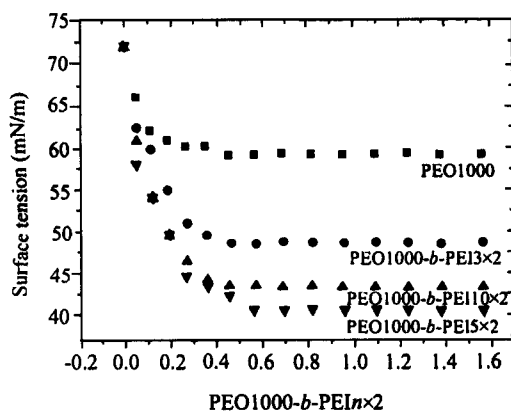


Fig. 5 Surface tension of the PEO1000-*b*-PEI copolymers.

As compared with fatty acid-based and multiply-substituted polyethylenoxide-amine materials, the current materials do show distinct surface tension behavior with their concentration. Fatty acid-based and multiply-substituted polyethylenoxide-amine derivatives show fairly constant surface tension values even at 10-fold concentrations due to their hydrocarbon content.¹³ The PEO-PEI materials of this report show a gradual decrease in their surface tension values with respect to concentration with surface tension values, dropping nearly 30% in the progression from 0.01% to 0.6% concentrations and displaying as much as a 38% decrease with respect to the parent PEO materials (Fig. 6).

Clay dispersancy of PEO-*b*-PEI copolymers

Previous success with highly ethoxylated polyamines¹⁶ prompted an investigation into the clay dispersancy behavior of PEO-PEI block copolymers having different molecular architectures. Using light-transmittance measurements of dispersed clay solutions at a constant pH (8.8) and at differing degrees of water hardness, an attempt to quantify the effects of specific PEI block lengths on clay dispersion was made.

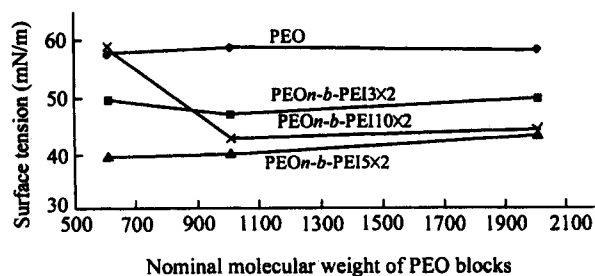


Fig. 6 Surface tension of copolymers as a function of PEO molecular weight (concentration of 1%, W/V).

As with surface tension measurements, PEO materials over a range of molecular weights were also analyzed. In the molecular weight range of 600 to 2000 Daltons, PEO had an essentially flat response (Fig. 7). Lower molecular weight copolymers (PEO-600- and PEO-1000-based series) also demonstrated clay dispersion values similar to the parent PEO materials. However, with the PEO-2000 series improvements are seen over the parent PEO material. Increased content of PEO units has been demonstrated to give better adsorption on mineral surfaces, including clays.¹⁷ Therefore, it appears that with PEO-PEI block copolymers a minimum PEO block size would be around 2000 daltons and even a small degree of PEI substitution is sufficient to give sizable improvements in clay dispersion. Increasing the PEI content within a PEO-PEI series does not produce a noticeable improvement in clay dispersion and may produce a slight detrimental effect. Clay dispersion in increasingly hard water (9 gpg as compared with 3 gpg) display the same tendency of the PEO, PEO600-PEI and PEO1000-PEI series and slightly less effective clay dispersancy for the PEO2000-PEI series.

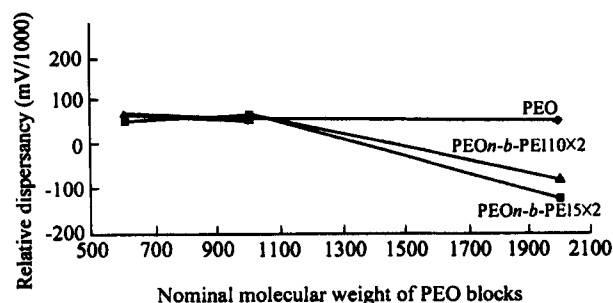


Fig. 7 Clay dispersancy by copolymers as a function of PEO molecular weight (copolymer concentrations of 5×10^{-5}).

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