

# Surface Active Block Copolymers: I. The Preparation and Some Surface Active Properties of Block Copolymers of Tetrahydrofuran and Ethylene Oxide

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## ABSTRACT

A new type of surface active block copolymer (TE type) having the general formula  $\text{HO}(\text{C}_2\text{H}_4\text{O})_x(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_y(\text{C}_2\text{H}_4\text{O})_z\text{H}$ , was obtained by addition of ethylene oxide to polyoxytetramethylene glycols with molecular weight of 1000-3400. TE types in which the polyoxyethylene sections comprised more than 20-25% of the total weight are soluble in water, and the relation between cloud point and oxyethylene content for TE types was similar to that for propylene oxide-ethylene oxide block copolymers (Pluronic). Some surface active properties of TE types were examined in comparison with those of Pluronic and some other surfactants. The surface tension, foaming and antifoaming properties of TE types were comparable to those of Pluronic. Although the wetting power of TE types was poor, their suspending power (for carbon black) was superior to that of Pluronic in both aqueous and nonaqueous media. The addition of TE types to some conventional detergents enhanced significantly their detergency. TE types showed a remarkable demulsifying action, on addition to some W/O emulsions.

## INTRODUCTION

According to the development of synthetic polymer chemistry, many types of polymers are being used as surfactants. Among others, nonionic surfactants having polyoxypropylene and polyoxyethylene groups as the hydrophobic and hydrophilic part respectively, known commercially as Pluronic, have received much attention with respect to their excellent wetting, dispersing, anti-foaming and demulsifying properties and have been reviewed recently (1). Similarly, butylene oxide has been used to build a hydrophobic base. Some attempts have been made to utilize other polyethers as hydrophobes. Furukawa and Oda (2) reported that the water soluble block copolymers of phenyl glycidyl ether and ethylene oxide (EO) did not exhibit any remarkable surface activity. Previously (3) the author reported the preparation of the block copolymers of alkyl ( $\text{C}_2$  to  $\text{C}_{12}$ ) glycidyl ethers and EO, and discussed the relation between the structure of hydrophobe and surface active properties.

Recently the utilization of the random copolymers from tetrahydrofuran (THF) and EO or propylene oxide as hydraulic fluids, lubricants and intermediates of polymeric elastomers has been described in some patents (4). How-

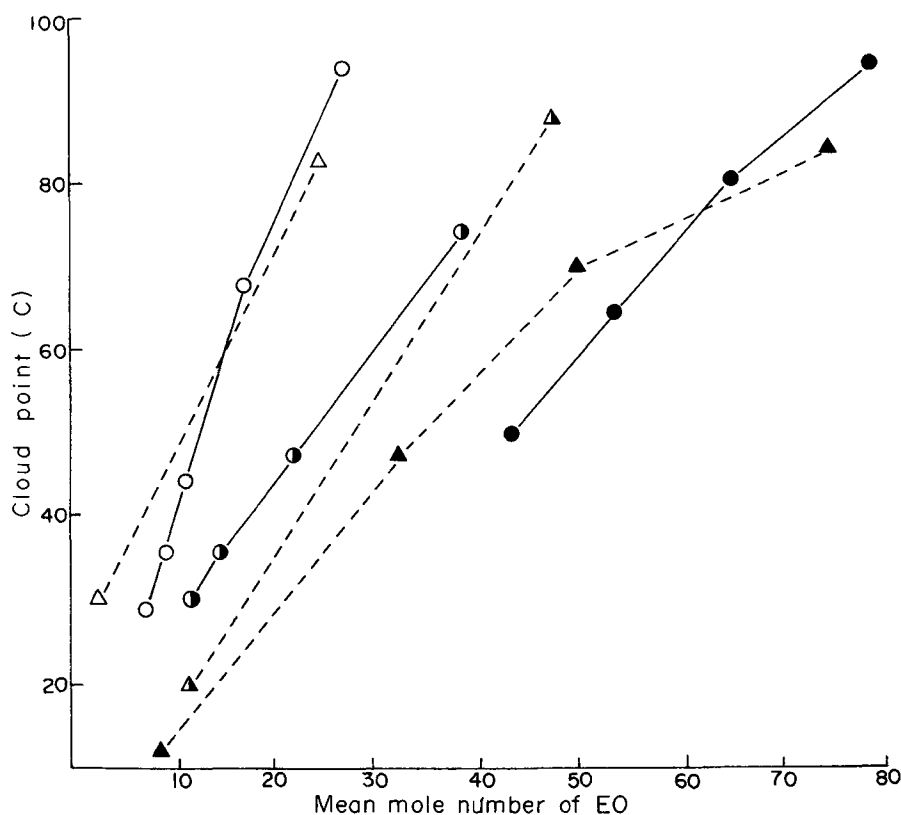


FIG. 1. Relation between cloud point and mean mole number of EO in surface active block copolymers. ○; T-100 series, ●; T-200 series, ●; T-340 series, △; Pluronic (molecular weight of the hydrophobe, 950) ▲; Pluronic (molecular weight of the hydrophobe, 2050) ▲; Pluronic (molecular weight of the hydrophobe, 3250)

TABLE I

Properties and Physical State of THF-EO Block Copolymers  $\text{HO}(\text{C}_2\text{H}_4\text{O})_x(\text{C}_4\text{H}_8\text{O})_y(\text{C}_2\text{H}_4\text{O})_z\text{H}^a$ 

Product	Mean M.W. of PTG	OE content wt %	$x+z^b$	Appearance of product	Melting point, C	Cloud point, C
T-100(17)	1000	16.8	4.5		25.0-28.5	<0
T-100(20)		20.0	5.7	White soft	27.0-29.5	<0
T-100(25)		25.0	7.6	waxy solid	27.0-30.0	27-29
T-100(30)		30.0	9.8		28.0-31.5	37-38
T-100(35)		35.0	12.0	white paste	---	44-45
T-100(43) <sup>d</sup>		43.2	17.0	white soft	26.0-28.5	67-68
T-100(54) <sup>d</sup>		53.7	26.5	waxy solid	27.5-29.5	93-94
T-100(60)		60.0	34.0	Light brown	32.0-34.0	>100
T-100(70)		70.0	53.0	waxy solid	32.0-34.0	>100
T-200(20)		2000	20.0	11.5		32.0-34.5
T-200(25)	25.0		15.0	White waxy solid	31.0-34.0	35-37 <sup>c</sup>
T-200(32)	31.9		21.5		32.0-34.0	46-47
T-200(45)	45.4		38.0		34.0-37.5	73-74
T-200(64)	64.3		82.0	Light brown waxy solid	42.5-46.0	>100
T-200(70)	70.0		106.0		48.0-49.5	>100
T-340(35)	3400	35.0	42.0		38.0-39.5	49-52 <sup>c</sup>
T-340(40)		40.0	52.0		38.5-40.0	62-65 <sup>c</sup>
T-340(45)		45.0	63.5		43.5-45.5	79-82 <sup>c</sup>
T-340(50)		50.0	77.5	White waxy solid	46.0-48.0	94-96 <sup>c</sup>
T-340(55)		55.1	95.5		49.0-51.5	>100 <sup>c</sup>
T-340(60)		60.0	116.5		50.5-52.5	>100 <sup>c</sup>
T-340(70)		70.2	183.0		55.5-57.0	>100 <sup>c</sup>
T-100(60) <sup>e</sup>	1000	(58.5)	(34)	Brown paste	---	41
T-200(60) <sup>e</sup>	2000	(60.0)	(70)	White paste	---	60

<sup>a</sup>Unless otherwise stated, all products listed here were prepared with the base-catalyzed method B.<sup>b</sup>Mean mole number of the added EO to PTG.<sup>c</sup>The aqueous solutions of these products are slightly turbid.<sup>d</sup>Prepared with the base catalyzed method A.<sup>e</sup>Prepared with the acid catalyzed reaction (method C).

ever, polyaddition of EO to THF polymer and the surface active properties of the resulting block copolymers have not yet been reported. The purpose of this investigation is to establish the polyaddition of EO to polyoxytetramethylene glycols in the presence of base or acid catalysts, to obtain information on the properties of the products in comparison with those of some known surface active copolymers (Pluronics, etc.) and to discuss the structural effects on the surfactant properties of block copolymers.

## EXPERIMENTAL PROCEDURES

### Materials

Polyoxytetramethylene glycols (PTG), having mean molecular weight 1000 (KAO Polyether T-100), 2000 (T-200) and 3400 (T-340), were employed as the starting materials. They were prepared by cationic polymerization of THF in the presence of a Lewis acid such as  $\text{BF}_3$  or  $\text{FSO}_3\text{H}$ . Their

TABLE II

Wetting Power of TE Types and Other Surfactants at 40 C

Surfactant	Sinking time, sec	
	0.5% <sup>a</sup>	0.05% <sup>a</sup>
T-100 (30)	334	1030
T-100 (43)	252	700
T-100 (60)	507	>1200
T-100 (70)	647	>1200
T-200 (32)	640	>1200
T-200 (45)	464	>1200
T-200 (64)	1350	>1200
Pluronic L-35	28	89
Pluronic P-84	45	115
Pluronic P-85	40	96
S-12 (61) <sup>b</sup>	1.2	26

<sup>a</sup>Concentration of solution.<sup>b</sup>EO condensate (OE content, 61%) of *n*-dodecyl alcohol.

IR spectra showed the presence of terminal OH groups. These PTG are white waxy solids and begin to melt at 20-25 C, are water-insoluble, and soluble in organic solvents other than hydrocarbons. EO was purified by distillation just before use.

### Polyaddition of EO

Polyaddition to PTG was carried out in the presence of a small amount of base or acid using the usual procedure. For the base-catalyzed reaction, two methods (A and B) were adopted.

*Method A.* The atmosphere in the reaction vessel was replaced with dry nitrogen gas. Then gaseous EO was conveniently introduced by bubbling it through the melted PTG in which 0.4% (by weight of PTG) of metallic potassium was dissolved. The reaction temperature was maintained at 165-175 C.

*Method B.* The autoclave was charged with PTG and 0.15-0.2% of metallic potassium, evacuated, filled with nitrogen gas and reevacuated. The vessel was heated to 120-130 C, and then the proper amount of liquid EO was added with stirring to relieve the vacuum and to provide the desired operating pressure. As the reaction began, EO was added to maintain the desired operating pressure. Thus the pressure was raised up to 28.5 psi during the reaction, and finally lowered to 14.2 psi after the absorption of the required amounts of EO.

After the reaction was completed, in both methods, the mixture was diluted with benzene and neutralized with alcoholic hydrochloric acid. The precipitated inorganic salt was removed by centrifugal separation, the azeotropic distillation with benzene was repeated to remove the water contained in the product, and benzene was carefully distilled off.

*Method C.*  $\text{BF}_3$ -ether complex was used as a catalyst in the acid-catalyzed reaction. The reaction is exothermic and was controlled by externally cooling the autoclave to maintain the temperature at 20-40 C. The reaction mixture

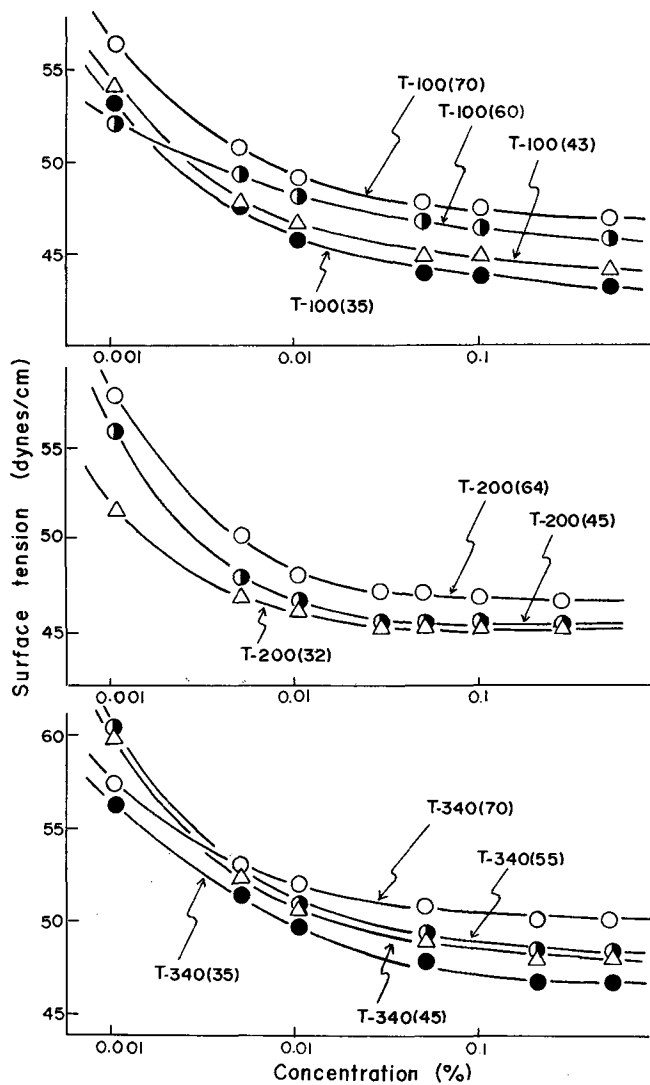


FIG. 2. Surface tension versus concentration curves for T-100, T-200 and T-340 series.

was treated as described above.

The approximate amount of the by-product, polyethylene glycol (PEG), in the products was estimated by a paper chromatographic analysis of the water layer separated from the aqueous solution of the product on warming above its cloud point.

#### Cloud Point

Cloud point of the product was measured on a 0.5% aqueous solution.

#### Surface Active Properties

**Surface Tension.** Surface tension was measured on a 0.05-1.0% aqueous solution with a Du Nouy tensiometer at 20 C.

**Wetting Power.** Sinking time was measured by the semimicro disc method (5) using cotton canvas disc (diameter, 1 in.) at 40 C.

**Foaming and Antifoaming Properties.** Foaming power was evaluated at 25 C by use of the method described by Yano et al. (6), which consisted of measuring the foam volume produced by bubbling 250 ml of air for 60 sec into 5 ml of the test solution. The antifoaming effect of copolymers on aqueous solution of anionic or nonionic foaming agent was examined by use of the following procedure. To 1% solution of sodium *n*-dodecyl sulfate or EO condensate of *n*-dodecyl alcohol, was added a small amount (0.01-0.1% by weight of the solution) of copolymer. The foam volume of the prepared sample solution was

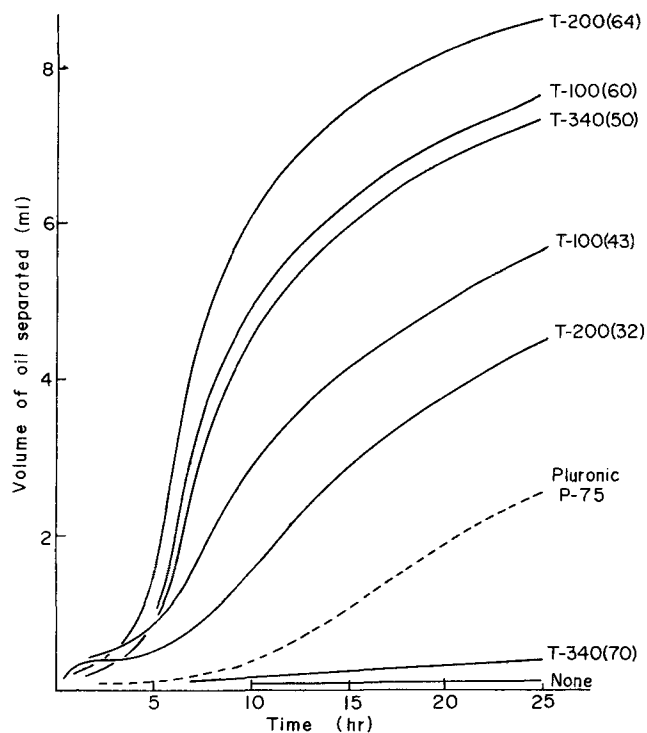


FIG. 3. Demulsifying action of block copolymers for water-in-kerosene emulsions.

measured at 25 C with the above method.

**Suspending Power.** By means of differential absorbance measurements, suspending power of copolymers for carbon black was determined in aqueous and nonaqueous media. For the test in water, 0.2 g of acetylene black (pretreated with benzene to remove organic materials and dried in vacuum) was added to 50 ml of 0.3% aqueous solution of the copolymer in a test tube (diameter, 20 mm) and allowed to stand at 30 C in thermo-controlled bath for 30 min to attain adsorption equilibrium. Then, the solution was shaken 20 times by up-ending for 1 min and allowed to stand at 30 C for 1 hr. From 5 cm depth below the liquid surface, 1 ml of the suspension was taken out and, as required, diluted with the same solution of copolymer as used for suspending. The optical density of the carbon suspension at 582  $\mu$  was measured with a photometer (Hitachi Spectrophotometer ESP-20). According to the method described by Mankowich (7), the equivalent concentration of black dye solution for each carbon suspension was estimated by use of the calibration line of Nigrosine Black. Suspending power of copolymers in benzene was also evaluated by the following procedure (8): to 20 ml of 1% solution of copolymer in benzene, 0.2 g of acetylene black as described above was added, shaken 100 times for 1 min and allowed to stand at 30 C for 30 min. Then, 0.5 ml of the suspension was taken out from the upper end, poured on the filter paper (Toyo 5C), and the solvent remaining on the paper was gradually evaporated. The reflectance of this paper was measured photometrically and compared with that of untreated filter paper. The reflectance measurements were carried out on the base of the reflectance of magnesium oxide.

**Detergency.** Detergency and additive effect on detergency of conventional detergents were measured by laundering artificially soiled cotton clothes with a mixture consisting of carbon black (0.8 g), hardened tallow (1.0 g), liquid paraffin (3.0 g) and carbon tetrachloride (800 g). The soiled clothes were used after aging for two weeks. The washing test was carried out by using a Launder-O-meter at 50 C without builders. The reflectance of the clothes before and after washing was determined.

TABLE III  
Foaming Power of TE Types and Other Surfactants at 25 C<sup>a</sup>

Surfactant	Concentration of solution, during 0 and 1 min							
	0.5%		0.3%		0.05%		0.005%	
	0	1	0	1	0	1	1	1
T-100(25)	0	0	---	---	0	0	0	---
T-100(30)	20	0	---	---	10	0	0	---
T-100(35)	20	0	---	---	15	0	5	0
T-100(43)	50	0	---	---	45	0	5	0
T-100(60)	65	-	---	---	65	0	5	0
T-100(70)	60	0	---	---	65	0	5	0
T-200(42)	---	---	20	0	10	0	0	---
T-200(45)	---	---	75	0	50	0	5	0
T-200(64)	---	---	45	0	50	0	5	0
Pluronic P-75	---	---	---	---	45	0	---	---
S-12(61) <sup>b</sup>	---	---	---	---	260	85 <sup>c</sup>	---	---
Emal O <sup>d</sup>	---	---	---	---	260	215 <sup>c</sup>	---	---

<sup>a</sup>Foam volume, milliliters.

<sup>b</sup>EO condensate (OE content, 61%) of *n*-dodecyl alcohol.

<sup>c</sup>Measured after standing for 5 min.

<sup>d</sup>Anionic surfactant (Kao Soap Co. product), *n*-C<sub>12</sub>H<sub>25</sub>OSO<sub>3</sub>Na.

**Demulsifying Action.** The demulsifying power of TE types and other copolymers were tested for water-kerosene and water-crude oil emulsions by the following procedure. The stable W/O emulsion was prepared from water and kerosene (volume ratio, 1:5) by use of isopropylamine salt of dodecylbenzene sulfonic acid as an emulsifier. To 25 ml of the emulsion (prepared just before use) in a graduated tube (diameter, 15 mm), was added 0.5 ml of 4% solution of copolymer in benzene. The test tube was shaken several times, allowed to stand at 30 C, and the volume of oil separated on the emulsion layer was recorded at time intervals. Water-crude oil emulsion (W/O, volume ratio, 1:1) was prepared without any emulsifier by addition of water to oil at 35 C over a period of 30 min under stirring with a propeller-type stirrer (300 rpm) and then continuing stirring for 1 hr. To 50 ml of the emulsion in a graduated tube, was added by use of micro-syringe 0.01 ml of 25% solution of copolymer in mixed solvent (methanol-xylene, volume ratio 1:1). Then, the test tube was stoppered, shaken 50 times by up-ending and allowed to stand at 40 C. After standing for 2 hr, the volume of water separated under the emulsion layer was read.

## RESULTS AND DISCUSSION

### Preparation of THF-EO Block Copolymers

The overall rates (g/min) of the EO addition to 50 g of PTG were 0.5-0.6, 1.2-1.6 and 2.5-2.9 for method A, B and C respectively, under the conditions described in the experimental section. This indicates that the reactivity of the terminal hydroxyl groups of PTG is comparable to those of usual primary alcohols. The by-product (PEG) content in the base-catalyzed reaction products never exceeded 5-6%. On the other hand, PEG content in the products obtained under acidic conditions went up to over 30-43%, as well as in EO additions to usual alcohols under the same conditions. To avoid coloring of products, the polyaddition of EO to PTG should be carried out with the autoclave method. Thus, the block copolymers soluble in water were derived from water-insoluble PTG without any trouble by the use of the conventional method for preparation of alcohol-EO adducts.

### Physical Properties

Some physical properties and the physical state of THF-EO block copolymers obtained are listed in Table I.

TABLE IV  
Antifoaming Power of TE and Pluronic Type Block Copolymers<sup>a,b</sup>

Foaming agent	Block copolymer	Amount of added block copolymer, during 0 and 5 min					
		0.01, wt %		0.03, wt %		0.1, wt %	
		0	5	0	5	0	5
Emal O <sup>b</sup>	T-100(25)	255	195	255	0	170	0
	T-100(43)	260	165	220	5	135	0
	T-200(25)	255	0	245	15	180	0
	T-200(45)	235	150	255	5	185	0
	T-340(35)	260	0	230	0	180	0
	T-340(55)	240	0	245	0	225	0
	Pluronic P-75	245	20	190	15	150	0
S-12(61) <sup>c</sup>	T-100(25)	260	35	265	25	265	50
	T-100(43)	265	35	265	45	260	65
	T-200(25)	265	35	265	35	265	75
	T-200(45)	260	40	265	45	265	65
	T-340(35)	255	120	255	75	255	55
	T-340(55)	255	250	255	60	260	50
Pluronic P-75	265	40	265	70	265	85	

<sup>a</sup>Foam volume, milliliters.

<sup>b</sup>Measured at 25 C for 1% solution of foaming agent containing a definite amount of block copolymer.

<sup>c</sup>See Table II.

TABLE V

Suspending Power of Block Copolymers for Carbon Black in Aqueous Medium<sup>a</sup>

Block copolymer	Carbon suspensibility <sup>b</sup> , mg/100 ml	
	A <sup>c</sup>	B <sup>d</sup>
T-100(43)	183	47
T-100(70)	184	---
T-200(32)	99	---
T-200(45)	126	42
T-200(64)	163	---
T-340(40)	45	---
T-340(45)	95	---
T-340(50)	108	---
T-340(60)	116	---
Pluronic L-35	0	4
Pluronic P-75	12	---
Pluronic P-77	90	---
Pluronic F-68	70	21

<sup>a</sup>Sample solutions (0.3%) were tested at 30 C.<sup>b</sup>The equivalent Nigrosine Black concentration.<sup>c</sup>A, acetylene black (average particle size, 42 m $\mu$ , pH, 6.8).<sup>d</sup>B, acetylene black (average particle size, 56 m $\mu$ , pH 7.1).

The physical state of TE types varied from semisolid to hard waxy solid with an increase in the molecular weight of starting hydrophobe and in the OE content of the product. The melting point increased gradually to near 60 C. TE types resemble Pluronics in physical properties. All the products are easily soluble in organic solvents such as alcohols, benzene, ether and carbon tetrachloride. The products of OE content above 20-25% are soluble in water and gave a transparent or slightly turbid aqueous solution. For the products of 20-60% OE content, a definite cloud point or range was observed. The cloud point range of the products having the lower OE content tends to become rather wide with an increase in the molecular weight of the hydrophobe, as can be seen in Table I. Also, it was observed that the heating rate affected greatly the cloud point or range of TE types, and very slow heating was required to obtain reproducible data. Figure I indicates the relation between the cloud point and the mean mole number of added EO for TE types prepared with method A and B, in comparison with those of Pluronics (1). Similar relationships hold for both types derived from the same molecular weight hydrophobes. In practice, when the OE content was adopted instead of the mole number of EO, the plots for all products of two types were approximately linear. On the basis of cloud point, no significant difference in water-solubility can be found between both types of the corresponding series. It is of interest that the hydrophobic

TABLE VI

Suspending Power of Block Copolymers for Carbon Black in Benzene<sup>a</sup>

Block copolymer	R <sup>b</sup> %	R <sub>0</sub> <sup>c</sup> - R, %
T-100(43)	75.2	16.6
T-100(70)	45.2	46.6
T-200(32)	83.4	8.0
T-200(45)	63.3	28.5
T-200(64)	42.5	49.3
Pluronic L-35	89.9	1.9
Pluronic P-75	89.8	2.0
Pluronic F-77	89.2	2.6
Pluronic F-68	88.9	3.4

<sup>a</sup>Sample solutions (1%) were tested using acetylene black A at 30 C.<sup>b</sup>Reflectance (%) of treated filter paper based on magnesium oxide.<sup>c</sup>Reflectance (%) of untreated filter paper based on magnesium oxide, 91.8%.

TABLE VII

Detergency of TE Types and Other Detergents for Cotton Cloth<sup>a</sup>

Surfactant	Concentration, %	D <sup>b</sup> , %
T-200(65)	0.1	40.5
Pluronic F-77	0.1	32.4
Emal O <sup>c</sup>	0.1	52.4
DBS <sup>d</sup>	0.1	48.6
T-200(65) +	0.02	53.2
Emal O	0.1	---
Pluronic F-77 +	0.02	44.3
DBS	0.1	---
T-200(65) +	0.02	57.5
DBS	0.1	---
Blanck	---	24.3

<sup>a</sup>Test condition, 50 times test solution by weight of soiled cloth was used in Launder-O-meter at 50 C for 30 min without builders.<sup>b</sup>D = (R<sub>w</sub> - R<sub>s</sub>)/(R<sub>0</sub> - R<sub>s</sub>).<sup>c</sup>See Table II.<sup>d</sup>Sodium dodecylbenzene sulfonate obtained by removal of salts from commercial product.

contribution of polyoxytetramethylene in TE block copolymers is almost the equivalent to that of polyoxypropylene of corresponding molecular weight, in spite of the difference in carbon and oxygen number of the hydrophobe. In the case of TE types the straight-chain structure and an increase in carbon number of the hydrophobe probably counteract each other in affecting the hydrophobic character.

Acid-catalyzed addition products give apparently an anomalous cloud point. However, by removing PEG (39%) from T-100(60') obtained with method C, (apparent cloud point, 41 C) net OE content estimated to be 32%, its cloud point came down to 35 C, close to that of T-100(30) prepared by the base-catalyzed reaction.

#### Surface Active Properties

*Surface Tension.* As can be seen in Figure 2, the minimum values of surface tension lie in the region of 42-50 dynes/cm, comparable to those of Pluronics, and the surface tension-log concentration curves for TE types have no clear inflection point. The surface activity decreased with an increase in the OE content. This trend is similar to that for the other types of copolymer nonionics. The methyl groups in the hydrophobic part of block copolymers are supposed to play an important role in their surface activity (3). From the viewpoint of structural effect on the properties, it is noticeable that the surface tension lowering ability of TE types are comparable to those of Pluronics in spite of containing no side chain in the hydrophobe of TE copolymers.

TABLE VIII

Demulsifying Power of Block Copolymers for Water-in-Crude Oil Emulsion<sup>a</sup>

Demulsifier	Crude oil		
	Minamiaga <sup>b</sup>	Kuwait	Kafgi
T-200(25)	88	90	100
T-200(30)	96	84	96
T-200(45)	84	76	94
APFR-EO A <sup>c</sup>	52	64	48
APFR-EO B <sup>c</sup>	80	8	22
Blanck	0	0	0

<sup>a</sup>Separated water per cent by weight of total water contained in initial emulsion.<sup>b</sup>One of Niigata oil fields in Japan.<sup>c</sup>Commercial products from alkylphenolformaldehyde resin and EO. OE content of A and B, 44% and 55% respectively.

**Wetting Power.** The sinking times found for 0.5-0.05% solutions of TE types were 5-20 min, while those of Pluronics and other conventional nonionics were 1-120 sec, as shown in Table II. According to the test method containing such a dynamic process as penetration, the wetting power of TE types was much lower than that expected from the surface tension data and very inferior to those of conventional nonionics. This fact suggests the lower diffusion rate of TE copolymers in aqueous solution owing to its high polymeric character.

**Foaming and Antifoaming Properties.** As shown in Table III, initial foam volumes of TE types were 0-70 ml, and the initial foams collapsed within a few minutes even at temperatures below their cloud points. Such remarkable low-foaming property is comparable to those of Pluronics known as representative low foamers. Also, the data in Table III indicate that in the two series of TE types, the initial foam volume passes through a maximum at a mole number of added EO. The maximum seems to correspond with critical hydrophile-hydrophobe balance proposed by Schick and Beyer who had found such maximum for polyoxyethylene glycol monoalkyl and monoalkylphenyl ether (9).

Table IV indicates that TE types are effective as an antifoamer for anionic detergent solution and rather inefficient for nonionic solution. The same behavior was also seen for Pluronics known as some of the most effective foam inhibitors.

There has been no clear explanation for the low-foaming property and the antifoaming mechanism established for nonionics of the block copolymer type. On the basis of the hydrophobe structure and the above-described results, however, some reasoning could be made as follows. Probably the hydrophobes of oxyalkylene type such as PTG and polyoxypropylene glycol are, more or less, subject to partial hydration in bulk and even in the surface layer of the solution. Such hydrophobic chains are considerably stretched to take the form of a loose coil, and formation of the close-packed film is prevented on adsorption of the block copolymer. Therefore, the low-foaming property could be explained in terms of the weaker cohesive force in the surface film and the restricted surface transport (10). The antifoaming effect of TE types on anionic detergent suggests that micellization and close-packed interfacial orientation of the detergent molecules are reduced owing to interaction with block copolymer.

**Suspending Power.** Table V and VI show the results in aqueous and nonaqueous media respectively. They indicate that the suspending power of TE types for carbon black is much greater than those of an analogous series of Pluronics. In T-200 series, stability of aqueous suspension increased stepwise with an increase in the OE content. This trend was also found in benzene suspension for both T-100 and T-200 series. Some benzene suspensions prepared with effective TE types were stable for periods exceeding three days.

**Detergency.** Results of washing tests are shown in Table VII. Detergency is expressed by the equation:  $D = (R_w - R_s) / (R_o - R_s)$ , where D indicates detergency (%),  $R_w$

and  $R_s$  are a reflectance of a soiled cloth after and before washing, respectively, and  $R_o$  is that of original clothes. Table VII indicates that detergency of TE type itself is rather moderate; however, TE type as an additive to conventional detergents is significantly effective on enhancing their detergency. This effect seems to be ascribed to its excellent suspending power for carbon. Thus, TE types appear to be utilizable as a promising additive for both increasing detergency and antifoaming, at least in detergent formulations for carbonaceous soils.

**Demulsifying Action.** As can be seen in Figure 3 and Table VIII, TE types exhibit far greater demulsifying power for W/O emulsions of hydrocarbons, in comparison with Pluronics and EO adducts of alkylphenol-formaldehyde resin which have been noted and practically used as effective demulsifiers. Also, Figure 3 shows that each series of TE types has an optimum OE content with regard to demulsification efficiency. Probably, this fact relates to its counteracting effect on the effective HLB of the emulsifier contained. While, it was found that TE types were also a valid demulsifier for reduced oil emulsions, they were some of the most difficult to separate efficiently; the data are not shown here. These results suggest that the high efficiency of TE block copolymers is related to the straight chain structure of their hydrophobe, favorable to hydration and adsorption on water droplets.

In this paper, some properties of TE types have been mainly compared with those of Pluronics. It could be concluded that similarity in the molecular structure of both types resulted in similar properties in many respects, while the structural changes in the oxyalkylene unit of the hydrophobe caused significant differences in some gross effects, probably owing to variation of the configuration in the solution and at the interface.

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