Radiation Curable, Micelle Forming, Block Copolymers as Soil Release Finishes for Polyester Fabrics

C. E. WARBURTON, JR.

Exploratory Polymer Research Department, Rohm and Haas Company, Spring House, Pennsylvania 19477

SYNOPSIS

Polyester fabrics were treated with aqueous solutions of block copolymers prepared from a polyethylene oxide diol, a diisocyanate, and 2-hydroxyethyl acrylate. The copolymers formed micelles in aqueous solution. Electron beam irradiation in the wet state produced fabrics with much improved release of oily soil on laundering.

INTRODUCTION

Polyester fabrics are oleophilic and hydrophobic. They hold oily soils tenaciously and do not readily release them on laundering. They can also be uncomfortable to wear, especially if the wearer is physically active. Perspiration and water vapor are not absorbed by the fibers, and hence transport to the garment surface is slow. A hydrophilic treatment enhances wicking of perspiration along fiber surfaces and through the fabric to the exterior of the garment where it can evaporate into the ambient air. A hydrophilic treatment may improve release of oily soil as well, but this is not always the case.

A number of hydrophilic treatments based on ethylene oxide functionality have been found to be beneficial on polyester fabrics. The most successful of these have been block copolymers of ethylene oxide and ethyleneterephthalate. Durability was attained by "cocrystallization"¹⁻³ or fiber penetration during high-temperature dyeing.⁴⁻⁶ In another type of treatment, polyethylene glycol dimethacrylates and diacrylates were exposed to high-energy ionizing radiation to induce polymerization, crosslinking, and grafting to fabric.⁷⁻⁹

The present work is concerned with electron beam irradiation of some interesting new materials designed and characterized by Dr. Donald B. Larson at Rohm and Haas Company.¹⁰ They are condensates of a polyethylene glycol of 2,000–20,000 molecular weight, a diisocyanate, and 2-hydroxyethyl

acrylate. There are both hydrophilic and hydrophobic segments in these block copolymers. In water, the hydrophobic segments tend to associate and micelles form. Such materials may therefore be referred to as "associative" copolymers. As a consequence of this association, the vinyl groups are sequestered in close proximity in the interior of the micelles, which enhances their rate of reaction on irradiation. Higher molecular weight starting materials can be used successfully when reactive groups are locally concentrated in this manner; in homogeneous solution, the fewer number of reactive groups would be too dispersed for the desired extent of reaction. Enhanced reactivity in micelles has been more generally discussed in the literature, e.g., Refs. 11 and 12. As a particular example, molecular weights of methyl methacrylate polymerized in sodium dodecyl sulfate micelles were 3 to 5 times higher than the corresponding values obtained during bulk polymerization; rates of polymerization, R_p , were 10-30 times faster.13

Some results with "nonfunctional" (i.e., no vinyl groups) materials are also relevant to the present work. When polyethylene oxide in solution was γ -irradiated, the polymer was crosslinked and the solution gelled.¹⁴ In contrast, γ -irradiation did not gel micellar solutions of *p*-octylphenoxypolyethoxy-ethanol (e.g., OPE 9-10, Triton X-100, Rohm and Haas); scission predominated, apparently because the PEO segments of the surfactant molecules were in a close-packed arrangement that prevented crosslinking.¹⁵

The urethane block copolymers used in this work were convenient to use. They were solid, stable ma-

Journal of Applied Polymer Science, Vol. 42, 207–215 (1991)

^{© 1991} John Wiley & Sons, Inc. CCC 0021-8995/91/010207-09\$04.00

terials that were generally readily water soluble. In contrast, commercially available polyethylene glycol dimethacrylates have limited water solubility. Because of their higher molecular weights, the urethane condensates are less volatile and possibly also less toxic than the PEG acrylates and methacrylates.

Release of oily soil was used as a measure of the utility of the copolymers as fabric treatments. It is a realistic, reliable, and discriminating test. Comfort is a much more nebulous property and cannot be assessed meaningfully by a simple laboratory test. Rate of water drop absorption or height of water rise by wicking are measures of hydrophilicity and water transport. These tests often do not show differences among fabric finishes of close chemical composition though. Variable adsorption of detergent and ions onto fabric during laundering can also confound subsequent tests of water absorption. In view of these experimental difficulties, soil release was used in this work as an initial screening test for product utility.

MATERIALS AND METHODS

Glossary of Acronyms and Trade Names

C_{12} EO	Ethoxylated lauryl alcohol, ~ 8700 equivalent weight			
DHPA	2,3-Dihydroxypropyl acrylate			
HEA	2-Hydroxyethyl acrylate			
HEMA	2-Hydroxyethyl methacrylate			
Hylene W	4,4'-Methylenebis (isocyanatocy- clohexane), DuPont			
PEG	Polyethylene glycol, Carbowax se- ries, Union Carbide Corporation. Number indicates approximate molecular weight			
PETA	Pentaerythritol triacrylate, Sartomer Company			
ТМР	Trimethylolpropane			

Polymer Synthesis

A sample polymerization procedure to produce 0.2 HEA/0.8 PEG 6000/1 Hylene W (equivalent proportions) copolymer was as follows:

A mixture of 122 g of Carbowax Polyethylene Glycol 6000 (3800 equiv wt), 150 g of toluene, and 0.13 g of dibutyltin dilaurate was heated in a flask to distill off the water-toluene azeotrope into a Dean Stark trap with upper layer return. When no more water was distilled over, the mixture was cooled to 60° C and 0.93 g of 2-hydroxyethyl acrylate was

added followed by 5.24 g of Hylene W. After 27 h at 60°C, the mixture was poured into a slab mold and air-dried.

Viscosity

Brookfield viscometer, Model LVTD, UL adapter, 14.68 s^{-1} shear rate.

Surface Tension

Fisher Surface Tensiomat, Model 21 (du Nouy method).

Fabrics

Testfabrics Style 767, Dacron 54 polyester woven, spun yarn. Testfabrics Style 9503, 50 polyester/50 cotton blend, woven. Testfabrics Style 361, Nylon 6 woven, spun yarn.

Pad-Bath Application to Fabric

Polymers were dissolved in sufficient water to provide the desired fabric add-ons. Solutions were typically 1.5-3% solids. When pentaerythritol triacrylate was used also, it was emulsified into the bath using a Waring blender. When bisphenol A was used, it was dissolved in an equal amount of acetone before addition to the bath. Fabrics were saturated in the bath solutions and passed through the rolls of a Birch Bros. padder at 1.9 mm/s (7.6 yd/min) and 206 mPa (30 psi) gauge pressure, two dips, two nips. The fabrics were sealed in polyethylene bags while awaiting irradiation.

Irradiation

Electron Beam

Fabrics were removed from sealed bags and were irradiated under nitrogen in an Electrocurtain processor, Model CB 200/30/20 (Energy Sciences, Inc., Woburn, Massachusetts), 195 kV, 157 mm/s (31 ft/min) line speed, at the doses shown in the tables of results. Two different irradiation procedures were used. In one, the fabric was subjected to half of the total dose, turned over, and then subjected to the remainder. In the other, the fabric was irradiated on one side only. The dose reported in the tables is the total dose applied to the surfaces of the fabrics. The fabrics were dried in a forced draft oven at 100°C for 5 min.

Ultraviolet Light

Fabrics were removed from sealed bags and passed on a conveyor belt in air through an Ashdee (Division of George Koch Sons, Inc., Evansville, Indiana) UV curing range with two 7.9-kW/m (200-W/ in.) mercury vapor lamps. The distance between the lamps and sample was 178 mm. When there were multiple passes, the fabric was turned over for each successive pass. A typical residence time was 1.7 s per pass at 228.6 mm/s (45 ft/min).

Fabric Add-On

Polymer add-ons were determined from weights of conditioned $(21^{\circ}C/65\% \text{ RH})$ fabrics before and after treatment, percent add-on = (final fabric weight – initial fabric weight) 100/initial fabric weight.

Soil Release

Soil release was measured using AATCC (American Association of Textile Chemists and Colorists) Test Method 130, "Soil Release: Oily Stain Release Method." The stain was dirty automobile crankcase motor oil diluted 10/1 with clean, unused oil. Fabrics were washed in a Maytag home washing machine, full-cycle wash, with hot (60°C) water, 100 g of Orvus Extra (sodium alkyl sulfate, Procter and Gamble) detergent, and eight terry towels for ballast. Fabrics were tested for soil release with no washes before staining and five washes before staining. The latter is a measure of the durability of the fabric treatment to laundering. A fabric sample with a 5 rating had the appearance of complete stain removal; a fabric sample with a 1 rating had the appearance of no stain removal.

RESULTS AND DISCUSSION

Colloidal Characteristics of Copolymers

Molecular weights and colloidal characteristics of two of the copolymers used in this work are reported in this section. The two copolymers were WM-5370A = 0.5 HEA/0.8 PEG 4000/1 Hylene W and CJC- 0938 = 0.5 HEA/0.5 methoxy PEG 5000/1 Hylene W.

Molecular weights determined by gel permeation chromatography of copolymers dissolved in tetrahydrofuran are shown in Table I. Molecular weights of CJC-0938 were higher than anticipated from the nominal composition. On a probability basis, the following proportions would be expected: 50% monofunctional polymer, 25% nonfunctional polymer, and 25% diacrylate diisocyanate. Thus, most polymer should be about 5000 molecular weight and some should be about 10,000. Gel permeation chromatography (GPC) though, indicates significant polymer in the 10^4 – 10^5 molecular weight range. It would seem that there was some polyethylene oxide diol in the reactants. Also, some polymerization may have occurred; the samples had aged for some time before GPC separation.

If these copolymers did in fact form micelles in aqueous solution, plots of surface tension or viscosity vs. concentration should provide evidence. Such plots are shown in Figures 1 and 2.

It is evident from Figure 1 that these materials were indeed surface active. Critical micelle concentrations appear to be in the 2-4% concentration range, which is confirmed by the change in slope of the viscosity vs. concentration curves in this range.

Turbidity was evident in CJC-0938 solutions at 0.1% and increased with further increases in concentration. WM-5370 solutions were clear across the concentration range.

The surface excess concentration, Γ , of WM-5370A was calculated from the slope of the curve in Figure 1 and the Gibbs equation to be 3.8×10^{-6} mol/m². The area per molecule was calculated to be 0.43 nm². The corresponding values for CJC-0938 were calculated to be 3.2×10^{-6} mol/m² and 0.52 nm², although these values may not be very meaningful because of the impurity of the material.

Soil Releasing Effectiveness of Various Associative Block Copolymers

Polyester fabric was padded through aqueous solutions of a number of associative urethane block co-

 Table I
 Average Molecular Weights and Molecular Weight Ranges

 of Copolymers

Copolymer	$ar{M}_n$	$ar{M}_w$	$ar{M}_w/ar{M}_n$	Molecular Weight Range
WM-5370A	14,100	37,300	2.64	$\frac{10^{3.1} - 10^{5.5}}{10^{3.4} - 10^{5.1}}$
CJC-0938	12,900	22,200	1.72	



Figure 1 Surface tension at 24°C vs. concentration of WM-5370A and CJC-0938.

polymers and electron beam irradiated. Soil release ratings are listed in Table II.

The results demonstrate that excellent soil release can be achieved, particularly using certain of these copolymers: CJC-0938, WM-5421B, WM-5368B, and WM-5370A, for example. (CJC-0938 and WM-5421B were samples of the same composition made by two different chemists.) Copolymers that were nominally monofunctional in 2-hydroxyethyl acrylate (CJC-0938 or WM-5421B—actually only par-



Figure 2 Viscosity at 24°C vs. concentration of WM-5370A and CJC-0938.

	Copolymer Composition (Equiv.)	Dose ^a (Mrad)		Add-on (%)	Soil Release Rating	
Sample Number			Irradiated on One Side or Two		Initial	Five Prewashes
WM-5421B	0.5 HEA/0.5 methoxy PEG 5000/1 Hylene W	2.5	2	2.0	4.7	5.0
CJC-0938	0.5 HEA/0.5 methoxy PEG 5000/1 Hylene W	2.5 2.5 2.5	2 2 2	1.9 0.8 0.3	4.4 3.5 1.0	5.0 4.2 2.7
WM-5368B	0.1 HEA/0.1 methoxy PEG 5000/0.8 PEG 6000/ 1 Hylene W	2.5 5 2.5 dry	2 2 2	2.0 2.2 1.8	3.5 4.2 1.5	4.7 4.5 1.0
WM-5370A	0.2 HEA/0.8 PEG 4000/1 Hylene W	2.5 5	2 2	1.8 1.8	$\begin{array}{c} 3.0\\ 3.7\end{array}$	4.7 4.5
COF-4248	0.2 HEA/0.8 PEG 6000/1 Hylene W	2.5 6	2 2	1.8 1.8	4.0 3.7	2.5 3.3
WM-5347A	0.2 HEA/0.8 PEG 20,000/1 Hylene W	2.5	2	1.2	1.3	1.0
WM-5360A	0.1 HEA/0.9 PEG 6000/1 Hylene W	2.5	2	1.6	4.3	1.2
WM-5341B	0.2 HEA/0.2 TMP/0.6 PEG 6000/1 Hylene W	$2.5 \\ 2.5$	2 1	1.9 1.6	3.7 3.9	4.0 3.7
WM-5341B + 10% PETA		2.5	1	1.6	3.9	3.7
WM-5421A	0.5 HEA/0.5 C ₁₂ EO/1 Hylene W	3	2	1.8	2.0	1.0
WM-5360C	0.4 HEA/0.6 PEG 6000/1 Hylene W	2.5 2.5 2.5	1 1 1	3.2 2.6 1.7	4.8 4.4 3.7	3.0 2.3 3.8
WM-5235A	0.2 HEMA/0.8 PEG 6000/1 Hylene W	2.5	1	2.0	4.0	3.7
WM-5237A	0.6 DHPA/0.5 PEG 6000/1 Hylene W	2.5	1	1.7	3.8	3.5
Untreated fabric		—	—	—	1.0	1.0

Table II Soil Release Ratings of Polyester Fabrics Treated with Various Associative Copolymers and Electron Beam Irradiated

* Fabrics irradiated wet except as indicated.

tially monofunctional, as discussed in the previous section), difunctional in 2-hydroxyethyl acrylate (WM-5370A), or branched (WM-5341B) were effective.

2-Hydroxyethyl acrylate was the reactive hydrophobe for most of the copolymers evaluated. Very good soil release ratings were also attained using 2hydroxyethyl methacrylate (WM-5235A) and 2,3dihydroxypropyl acrylate (WM-5237A). The acrylate functionality in WM-5237A was distributed along the copolymer backbone as well as at the ends. In other words, there were "internal" reactive hydrophobes in this copolymer. Its molecular weight was relatively high also, as judged by solution viscosity.

WM-5421A was similar to WM-5421B except that ethoxylated lauryl alcohol was used instead of methoxy PEG 5000. Soil release ratings were only marginally improved by WM-5421A. The hydrophobic lauryl component in the polymer was therefore detrimental. The alkyl chain segments may have shielded vinyl groups from each other. Also, the number of molecules per micelle, and consequently the concentration of reactive groups per micelle, may have been reduced. Either shielding or reduced concentration would have reduced extent of reaction and molecular weight buildup. The alkyl chain segments may also have harmed soil releasing effectiveness.

The length of the polyethylene oxide hydrophile chain was important. Soil release was not significantly improved when the molecular weight of the polyethylene oxide was 20,000 (WM-5347A), but it was appreciably improved when the molecular weight was 4000 or 6000. When polyethylene oxide molecular weight was too high, there was probably too low a concentration of vinyl groups to build molecular weight, crosslink, and graft to polyester. The irradiated product may have been too water soluble.¹⁶

Initial soil release with WM-5360A (0.1 HEA/ 0.9 PEG 6000/1 Hylene W) was good, but durability was poor. This copolymer required a long time to dissolve in water, as did the branched copolymer WM-5341B. The lower proportion of reactive HEA in WM-5360A was probably responsible for poor durability.

WM-5360C (0.4 HEA/0.6 PEG 6000/1 Hylene W) was a difunctional copolymer with a relatively high proportion of HEA and hence lower molecular

weight. Initial soil release ratings were excellent, but durable soil release ratings varied widely in repeated evaluations, from 2.3 to 3.8.

Results were similar when fabrics were irradiated on one side vs. both sides. The radiation apparently penetrated the fabric sufficiently to initiate reaction on the other side. A 5- or 6-Mrad dose was no more effective than 2.5 Mrad. Running at twice the speed and current to maintain the same dose produced essentially equivalent soil release ratings (data not shown).

Soil release ratings tended to drop below 4 when fabric add-on was less than 1%.

A fabric sample treated with WM-5368B was dried before electron beam irradiation. Soil release improvement was only minuscule.

Polyester fabric was padded through solutions of WM-5421B (0.5 HEA/0.5 methoxy PEG 5000/1 Hylene W) or WM-5421B + 10% pentaerythritol triacrylate (on weight of WM-5421B). The trifunctional PETA would be expected to help insolubilize the WM-5421B on irradiation. Some fabrics were irradiated while still wet after padding; others were dried first and then irradiated. Excellent soil release ratings were achieved with or without PETA when the fabrics were irradiated wet (Table III). Doses from 1.5 to 20 Mrad were effective. The PETA did not appear to be of significant benefit; sufficiently high degrees of polymerization and insolubilization were attained without it. As with WM-5386B, irradiation of dried fabrics was ineffective in improving soil release ratings.

		Dose (Mrad)	Add-on (%)	Soil Release Rating		
РЕТА	Fabric State when Irradiated			Initial	Five Prewashes	
+	_	0	5.1	1.0	1.0	
+	Dry	5	5.1	1.0	1.0	
+	Dry	10	5.1	1.0	1.0	
+	Dry	20	5.1	1.0	1.0	
+	Wet	1.5	2.3	3.0	4.3	
+	Wet	2.5	1.5	4.0	4.3	
+	Wet	5	1.5	3.0	3.5	
+	Wet	5	5.0	4.8	4.5	
+	Wet	10	4.3	4.8	4.5	
+	Wet	20	6.9	4.8	4.0	
_	Wet	2.5	2.0	4.7	3.5	
-	Wet	2.5	2.0	4.7	5.0	

Table IIISoil Release Ratings of Polyester Fabrics Treated with WM-5421B*+ Pentaerythritol Triacrylate and Electron Beam Irradiated

* 0.5 HEA/0.5 methoxy PEG 5000/1 Hylene W copolymer.

Fabric	Soil Release Agent	Dose (Mrad)	Add-on (%)	Soil Release Rating	
				Initial	Five Prewashes
Nylon 6	CJC-0938	2.5	1.3	4.2	4.7
	None		_	1.0	2.0
50 Polyester/50 cotton	CJC-0938*	2.5	0.85	3.3	3.3
	COF-4248 ^b	6	1.4	3.5	3.5
	None	—		2.0	3.0

Table IVSoil Release Ratings of Nylon and Polyester/Cotton Fabrics Treatedwith Associative Copolymers and Electron Beam Irradiated

^a 0.5 HEA/0.5 methoxy PEG 5000/1 Hylene W copolymer.

^b 0.2 HEA/0.8 PEG 6000/1 Hylene W copolymer.

Soil Releasing Effectiveness on Nylon and Polyester/Cotton Fabrics

A nylon fabric and a polyester/cotton blend fabric were padded through solutions of copolymers listed in Table IV and electron beam irradiated. Soil release ratings of the nylon fabric were improved substantially by treatment. Soil release ratings of the polyester/cotton blend fabric were also improved, but to a lesser degree than with polyester or nylon. This was anticipated because polyethylene oxide type finishes have generally been ineffective in improving soil release of cotton and polyester/cotton blend fabrics.

Exposure to High Temperatures

Soil release ratings were sometimes diminished when fabrics were exposed to simulated, rather severe heat setting conditions of 220°C for 1–2 min following EB irradiation and drying (Table V). Fabric addons were sometimes reduced also. Polyethylene oxides readily form peroxides. Apparently polymer degradation occurred and in some instances some low molecular weight material vaporized. Fabric hand was limper and drops of water were absorbed more rapidly. These changes were consistent with oxidative degradation of the soil release agent to lower molecular weight, more water soluble polymer.

Bisphenol A (4,4'-isopropylidenediphenol, Aldrich Chemical Co.) was an effective antioxidant. At 1% on weight of soil release polymer, weight gain and soil release ratings were maintained on exposure to 220°C for 1 min (Table V).

Soil Releasing Effectiveness of PEG Acrylates and Dimethacrylates

A number of PEG diacrylates and dimethacrylates from commercial sources were evaluated. All were essentially ineffective except for PEG 200 diacrylate, which produced excellent soil release (Table VI).

Reasons for the failure of the other diacrylates and dimethacrylates are speculative. The proportion of vinyl functionality in the higher molecular weight compounds may have been too low for sufficient ex-

		Add-on (%)	Soil Release Rating		
Antioxidant	220°C for 1 min		Initial	Five Prewashes	
None	_	0.7	3.5	2.0	
	+	0.2	3.2	2.5	
	-	2.5	4.0	4.3	
	+	2.6	3.8	3.0	
Bisphenol A ^b	-	1.7	4.8	4.0	
_	+	1.7	4.0	4.2	

Table V Effect of 220°C and Antioxidant on Soil Release*

* Polyester fabric, 0.5 HEA/0.5 methoxy PEG 5000/1 Hylene W copolymer (CJC-0938) 2.5 Mrad wet, one side of fabric.

^b 1% on weight of CJC-0938.

	Polymer composition	Irradiated Wet or Dry	Add-on (%)	Soil Release Rating	
Supplier				Initial	Five Prewashes
Sartomer	PEG 200 diacrylate	Wet	1.7	4.5	4.8
		Dry	1.7	3.0	3.0
Polysciences	PEG 400 diacrylate	Wet	0.4	1.0	1.0
		Dry	0.2	1.0	1.0
Sartomer	PEG 200 dimethacrylate	Wet	4.2	2.0	1.0
	-	Dry	3.4	1.0	1.0
Sartomer	Tetraethylene glycol	Wet	7.6	2.0	1.0
	dimethacrylate	Dry	1.2	1.2	1.0
Polysciences	PEG 600 dimethacrylate	Wet	1.8	1.3	1.0
		Dry	2.0	2.0	2.0
Union Carbide	PEG 6000	Wet	2.3	1.0	1.0
		Dry	2.5	1.0	1.0

 Table VI
 Soil Release Ratings of Polyester Fabrics Treated with Polyethylene Glycol Diacrylates and

 Dimethacrylates and Electron Beam Irradiated^a

^a 2.5 Mrad dose, fabrics irradiated on both sides.

tent of reaction. PEG 200 dimethacrylate may have been less reactive than the diacrylate and may have degraded more. Lower water solubility may also have been a factor. (The dimethacrylate bath solutions were opaque, whereas the diacrylate bath solutions were clear.) The low add-ons with PEG 400 diacrylate were not intended. The same bath concentration used for the other materials produced low add-ons (< 0.5%) and no improvement in soil release. The low add-ons for PEG 400 diacrylate shown in Table VI were attained using triple the normal bath concentration. There was apparently extensive degradation and volatilization. The commercial products discussed may have contained different levels of impurities (e.g., hydroperoxides, metallic ions) that accelerated degradation more in some products than others. PEG 6000, a nonfunctional control, was ineffective.

UV Irradiation

Samples of polyester fabric were padded through solutions of WM-5421B. A photoinitiator, α , α -diethoxyacetophenone (Union Carbide Corp.) was used at 2% on weight of bath solids. The photoinitiator absorbs UV light and initiates a free radical reaction that polymerizes the micelle.

Fabrics were passed in air under UV lamps varying numbers of times at various speeds ranging from one pass at 457 mm/s (90 ft/min) to three passes at 76 mm/s (15 ft/min). Some fabrics were irradiated while still wet; some were dried (100°C for 5 min) before irradiation. Some were irradiated both wet and dry. Addition of 10% pentaerythritol triacrylate on weight of WM-5421B solids was also evaluated.

For all the UV cure schemes, soil release ratings were no better or only slightly better than the control. The reason for the failure of UV irradiation to impart soil release is not known. Polymerization undoubtedly occurred.¹⁰ A possible explanation was UV degradation in the polyethylene oxide blocks, which reduced molecular weight and abetted removal in laundering. Polyethylene oxide is known to degrade readily on absorption of energy from UV irradiation.¹⁷ Also, significant grafting to fabric may have occurred on electron beam irradiation but not on UV irradiation. Polyethylene terephthalate is a difficult substrate to graft to and is relatively resistant to UV attack.

Redox and Thermal Initiation

Polyester fabrics were padded with solutions of 0.5 HEA/0.5 methoxy PEG 5000/1 Hylene W copolymer (WM-5421B or CJC-0938). The solutions contained either a cumene hydroperoxide/isoascorbic acid/Fe²⁺ redox polymerization initiator system or an ammonium persulfate thermal polymerization

system. Fabric samples were sealed in polyethylene bags and held at 23–93°C for various periods of time.

Bath solutions were subjected to the same thermal conditions as fabrics. The solutions gelled after a few minutes indicating that polymerization in fact occurred.

Dry fabric add-ons of 1-7% generally did not produce a significant improvement in soil release, regardless of temperature-time polymerization conditions. In a couple of seemingly random instances, initial ratings were excellent, 4.9-5.0, but durable ratings were still poor, 1.0-1.3.

An explanation for the failure of redox and thermal initiation to produce good soil release must again be speculative. It was most likely a consequence of degradation in the ethylene oxide chain segments and a paucity of grafting to polyester fabric.

CONCLUSIONS

Electron beam irradiation of polyester fabrics treated with aqueous solutions of certain block copolymers comprising ethylene oxide segments and reactive hydrophobes produced excellent durable soil release. The reactive groups were concentrated in the interior of micelles, which enhanced the rate and degree of reaction on irradiation. It was essential that the fabrics be irradiated before drying.

UV and chemical (thermal or redox) initiation were ineffective in improving soil release.

Exposure to excessive heat was detrimental and should be avoided. If necessary, bisphenol A, and possibly other antioxidants, can be used to protect the finish against degradation under such conditions. Dr. D. B. Larson provided helpful background information. Mr. W. J. Meyer and Dr. C. J. Chang synthesized the copolymers.

REFERENCES

- 1. J. E. McIntyre and M. M. Robertson, U. S. Pat. 3,416,952 (December 17, 1968).
- D. A. Garrett and P. N. Hartley, J. Soc. Dyers Colour, 82, 252 (1966).
- 3. J. A. Moyse, Text. Inst. Ind., 8(2), 43 (1970).
- 4. C. A. Ferguson, Am. Dyest. Rep., 71(6), 43 (1982).
- 5. A. Tropea, U. S. Pat. 4,346,130 (August 24, 1982).
- W. K. Larson, M. M. Lynn, and E. S. McAllister, U. S. Pat. 4,330,588 (May 18, 1982).
- I. Sakurada, T. Okada, and Y. Shimano, U. S. Pat. 3,779,881 (December 18, 1973).
- 8. J. J. Baron, U. S. Pat. 3,794,465 (February 26, 1974).
- T. Okada, Y. Shimano, and I. Sakurado, U. S. Pat. 3,926,551 (December 16, 1975).
- 10. D. B. Larson, Rohm and Haas Co., internal development.
- E. H. Cordes and R. B. Dunlap, Acc. Chem. Res., 2, 329 (1969).
- N. J. Turro and W. R. Cherry, J. Am. Chem. Soc., 100(23), 7431 (1978).
- D. J. Lougnot and J. P. Fouassier, Makromol. Chem. Rapid Commun., 4, 11 (1983).
- 14. J. Stafford, Makromol. Chem., 134, 57 (1970).
- A. A. R. Al-Saden, A. T. Florence, and T. L. Whateley, *Colloids Surf.*, 2, 49 (1981).
- C. E. Warburton and F. J. Parkhill, *Text. Chem. Color*, 5(6), 113 (1973).
- 17. C. W. McGary, Jr., J. Polym. Sci., 46, 51 (1960).

Received January 31, 1990 Accepted March 21, 1990