THE ADSORPTION BEHAVIOR OF POLYSTYRENE-POLY (METHYL METHACRYLATE)
MIXTURES CONTAINING BLOCK COPOLYMERS

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INTRODUCTION

The preparation and characterization of block copolymers has been actively pursued in recent years (1). Although such copolymers have been recognized as unique interface active species, their behavior at solid/liquid interfaces has received relatively little attention. Accordingly, a study has been made of the adsorption behavior of samples containing S/MMA block copolymers of the AB type. The styrene/methyl methacrylate (S/MMA) system was chosen because the adsorption behavior of S and MMA homopolymers has been studied, both as individual polymers and as mixtures (2). Since the S/MMA block copolymer synthesis procedure consistently yielded a mixture of S and MMA homopolymer plus S/MMA block copolymer, all measurements thus far have been confined to such mixtures.

EXPERIMENTAL

S/MMA block copolymerizations were carried out in toluene at -78°C after the method of Cunningham and Treiber (3) and with n-butyl lithium as catalyst. All transfer operations were carried out in a glove box (argon atmosphere). Anionic S (PS-l) and MMA (PMMA-l) homopolymers were similarly prepared with n-butyl lithium as catalyst. The anionic PMMA homopolymer had a J value of 56 which indicates it has a large degree of isotacticy (4). Free radical PMMA (PMMA-2) was prepared in bulk at 60°C with n-dodecyl mercaptan as chain transfer agent to control molecular weight and a, b-bisisobutyronitrile as initiator. The homopolymers and S/MMA block copolymer samples were isolated by precipitation into methanol and freeze dried from benzene. After isolation, a portion of sample C was reprecipitated into n-heptane from benzene and then extracted.
briefly with acetonitrile, a solvent for MMA homopolymer and non-
solvent for S homopolymer. This treatment yielded Sample C-1.
Brief extraction of sample C-1 with methylcyclohexane (C₆H₁₂CH₃),
a solvent for S and nonsolvent for MMA homopolymer, yielded
sample C-2. Sample A was extracted with C₆H₁₂CH₃ to give two frac-
tions, A-1 (C₆H₁₂CH₃ soluble) and A-2 (C₆H₁₂CH₃ insoluble). Fraction
A-1 was isolated by precipitation into n-heptane. Fraction
A-2 was extracted with dimethylsulfoxide (DMSO) to yield two frac-
tions, A-3 (DMSO soluble) and A-4 (DMSO insoluble). Fraction A-3
was isolated by precipitation into isopropanol. All fractionated
samples were freeze dried from benzene. In all cases, the effective-
ness of the extractions was limited due to the formation of stable
colloidal dispersions.

Table I contains conversions of the various polymerization
reactions, catalyst concentrations, and number

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conversion, %</th>
<th>Catalyst Conc.,*</th>
<th>Mₙ</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>58.2</td>
<td>0.8</td>
<td>27,400</td>
</tr>
<tr>
<td>A-1</td>
<td>-</td>
<td>-</td>
<td>37,200</td>
</tr>
<tr>
<td>A-3</td>
<td>-</td>
<td>-</td>
<td>37,900</td>
</tr>
<tr>
<td>A-4</td>
<td>-</td>
<td>-</td>
<td>39,500</td>
</tr>
<tr>
<td>B</td>
<td>61.8</td>
<td>1.4</td>
<td>22,200</td>
</tr>
<tr>
<td>C</td>
<td>75.4</td>
<td>2.0</td>
<td>22,700</td>
</tr>
<tr>
<td>C-1</td>
<td>-</td>
<td>-</td>
<td>31,700</td>
</tr>
<tr>
<td>C-2</td>
<td>-</td>
<td>-</td>
<td>70,200</td>
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<tr>
<td>PS-1</td>
<td>97</td>
<td>0.6</td>
<td>38,100</td>
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<tr>
<td>PMMA-1</td>
<td>35</td>
<td>1.0</td>
<td>80,000</td>
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<tr>
<td>PMMA-2</td>
<td>25</td>
<td>(Free Radical)</td>
<td>55,000</td>
</tr>
</tbody>
</table>

* per 15 g. monomer used

average molecular weights (Mₙ) for all samples. Values of Mₙ were
determined in toluene (37°C) with a Hewlett-Packard Model 502 high
speed membrane osmometer (Hewlett-Packard Corporation, North Holly-
wood, California). Gel permeation chromatography analyses indicate
all block samples have comparatively narrow molecular weight dis-
tributions.

Procedures for construction of the polymer adsorption isotherms