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AMPHIPHILIC GRAFT COPOLYMERS AS PHASE-TRANSFER CATALYSTS IN A SOLID-LIQUID SYSTEM†

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ABSTRACT

Amphiphilic graft copolymers consisting of a hydrophobic backbone and poly(oxyethylene) (PEO) side chains were employed as solid-liquid phase-transfer catalysts (PTC) in the substitution of octylbromide by solid potassium phenoxide in toluene. A wide variety of structures were synthesized via ester substitution of poly(phthalimidoacrylate) (PPIA) or poly(phthalimidoacrylate-*co*-styrene) [poly(PIA-*co*-St)] with amino-functionalized methoxy-PEO (MPEO-NH_2). The phase-transfer catalytic activity (PTA) of these soluble graft copolymers was studied as a function of the structure of the backbone, the length of the side chains, and the graft density. The graft copolymers of a high degree of grafting showed PTA higher than that of parent PEOs. GPC was used to study the behavior of the graft copolymers in toluene at 90°C. It is believed that the phase-transfer reaction is accelerated in the PEO microphase.

†Dedicated to Prof. Ivan Panayotov on the occasion of his 70th birthday.

INTRODUCTION

For years it has been well known that phase-transfer catalysis is a powerful method to perform interactions between reagents located in two distinct phases. The species which enables the reaction to proceed by transferring the reagent from one phase to another acts as a phase-transfer catalyst. The great possibilities offered by this method stimulated the search for new catalytic systems whose activity appeared to be highly dependent on their nature, molecular characteristics, and the type of reaction: solid–liquid or liquid–liquid.

Poly(oxyethylene) (PEO) and its derivatives were found to be active phase-transfer catalysts (PTCs) due to their ability to complex alkaline cations [1]. They exert an acceleration effect on many nucleophilic reactions [2, 3], and in some cases their phase-transfer catalytic activity (PTA) has been found to be superior to the activity of the well-known crown ethers [4].

The mechanism of action of soluble PEO derivatives, block and star-shaped copolymers, under solid–liquid and liquid–liquid conditions has been the object of many studies [5–10]. In solid–liquid reactions they have two possible functions: to solubilize the solid salt reagent and to enhance the nucleophilicity of the anion. These phenomena are dependent on both the structure and composition of the PTCs [8–12]. Block, graft, and star-shaped copolymers consisting of a hydrophobic moiety and PEO chains showed higher catalytic activity in the Williamson ether synthesis than linear PEO [6, 9, 10, 13]. An important variable in these studies was the molecular weight of the constituent blocks, but the results obtained with catalysts of different architectures showed contradictory molecular weight–PTA relationships [3, 6, 10, 11]. When linear PEOs were used as metal ion complexation agents, it was accepted that the interaction of the ether oxygens with the alkali ions proceeds intramolecularly and the cation binding constants increase with increasing polyether chain length [14, 15]. But in phase-transfer catalysis the complexation ability of PEOs appeared to be only one of the factors determining their PTA. The thermodynamic compatibility of PEO derivatives with the solvent, their ability to form aggregates, the accessibility of the activating groups, and specific interactions between the anion and the catalyst were considered as important factors in phase-transfer catalysis by PEO-based materials [6, 10, 11, 13].

The aim of the present work was to study the PTA of amphiphilic graft copolymers consisting of a hydrophobic backbone and PEO side chains in the reaction of solid potassium phenoxide with *n*-octyl bromide in toluene. The interest to these materials arose from their ability to undergo microphase separation that endows them with properties not possessed by the parent homopolymers. We examined a wide range of graft copolymers of varying composition, length of the side chains, and graft density, and compared their PTA with that of linear PEOs.

EXPERIMENTAL

Materials

1-Bromooctane and phenylcyclohexane (purchased from Fluka AG) were distilled under reduced pressure. Potassium phenoxide was prepared by the method of

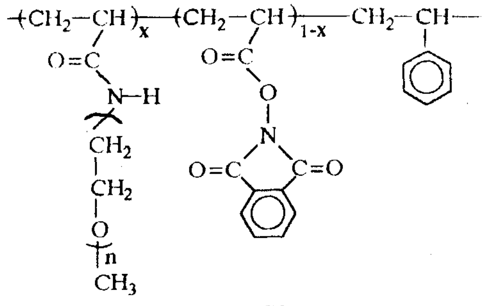
Kornblum and Lurie [16]. Graft copolymers were synthesized via ester substitution of polymeric activated esters with MPEO-NH_2. In our previous paper [17] we showed that polyphthalimidoacrylate and the copolymer poly(phthalimidoacrylate-*co*-styrene), which was found to be of alternating structure, are suitable for the preparation of the amphiphilic graft copolymers shown in Scheme 1. To purify the products, solutions of the graft copolymers were filtered through respective molecular weight cutoff Millipore membranes. ^1H NMR enabled the compositional determination of the graft copolymers by comparing the resonances for the aromatic phthalimido and styrene protons with that for the oxyethylene protons. The extent of activated ester substitution, the PEO content, and the average number of backbone monomer units between two grafts were calculated and are summarized in Table 1. The designations 1G and 2G refer to graft copolymers having a homopolymer and copolymer backbone, respectively. The diblock copolymer, comprising a polyisoprene and PEO blocks, both of molecular weight 5000, was prepared by sequential anionic polymerization of isoprene and ethylene oxide.

The behavior of the graft copolymers in toluene was studied by GPC at 90°C (Waters 150C, μ-Styragel columns).

Williamson Ether Synthesis

$$\text{PhOK(solid)} + n\text{C}_8\text{H}_{17}\text{Br(toluene)} \xrightarrow[\text{reflux}]{\text{catalyst}} \text{C}_8\text{H}_{17}\text{OPh} + \text{KBr}$$

The Williamson synthesis was run in a two-neck flask fitted with a stirring paddle, reflux condenser, and a sampling port. It was charged with a graft copolymer containing 1.022 mmol oxygen atoms and 3 mL of 2.4 M toluene solution of *n*-octyl bromide (0.72 mmol) containing 0.7 mmol phenylcyclohexane as internal



G1,G2

Graft copolymer	Backbone
1G	PPIA
2G	Poly(PIA-co-St)

SCHEME 1. Structure of the amphiphilic graft copolymers.

TABLE 1. Structure and Phase-Transfer Activity of Amphiphilic Graft Copolymers in the Reaction of 1-Bromooctane with Solid Potassium Phenoxide in Toluene at 90°C[a]

PTC					Williamson reaction	
		PEO				
Code[b]	x[c]	M_n	Content, wt%	Backbone units per PEO graft	Yield,[d] %	k_{obs} ($\times 10^4$), s^{-1}
1G47	0.2	2000	70	3.8	70	1.16
1G48	0.32	2000	80	2.0	83	1.72
1G49	0.55	2000	90	0.8	88	1.86
1G50	0.97	2000	96		93	2.22
2G66	0.24	750	40	7.0	50	0.66
2G61	0.35	750	50	4.6	53	0.75
2G64	0.48	750	60	3.2	62	0.80
2G63	0.65	750	70	2.0	70	0.93
2G62	0.90	750	80	1.2	70	1.02
2G65	0.95	750	82	1.0	72	1.11
2G55	0.10	2000	40	19.4	50	0.54
2G51	0.15	2000	50	12.4	57	0.68
2G52	0.21	2000	60	8.4	59	0.67
2G54	0.48	2000	80	3.0	69	0.98
2G56	0.83	2000	90	1.4	75	1.10
2G58	0.95	2000	92	1.0	87	1.70
2G76	0.06	5000	50	31.0	71	1.00
2G74	0.20	5000	80	8.0	92	2.23
MPEO-750-NH_2					66	0.83
MPEO-2000-NH_2					82	1.30
MPEO-5000-NH_2					97	2.72
Polyisoprene-PEO[e]					96	2.72

[a] 3 mL toluene solution of $C_8H_{17}Br$ (0.72 mmol), PhOK (2.1 mmol), graft copolymer (1.022 mmol of oxygen).

[b] 1G refers to a homopolymer backbone, 2G to a copolymer backbone (Scheme 1).

[c] Mole fraction of substituted activated ester.

[d] After 3 hours.

[e] Each block had a molecular weight of 5000.

standard. The mixture was refluxed with stirring, and potassium phenoxide (2.1 mmol) was added at zero time. The reaction was monitored by quantitative gas-liquid chromatography (Carlo Erba, model Fractovap 4100 with a capillary column). The pseudo-first-order rate constants were obtained by plotting $\ln([\mathrm{OctBr}]_0/[\mathrm{OctBr}]_t)$ versus time and computed by the least-squares method.

RESULTS AND DISCUSSION

GPC in Toluene

GPC studies in toluene at 90°C showed a peculiar behavior of the amphiphilic graft copolymers which was markedly dependent on their composition. PEO homopolymers, diblock copolymers, and graft copolymers of type 2G, being of a low degree of grafting, were eluted under these conditions as molecularly dissolved species. On the contrary, GPC traces of the graft copolymers comprising a homopolymer backbone with a PEO side chain (polymers 1G) were polymodal with a considerable fraction of species of large hydrodynamic volume (Fig. 1a). Similar behavior was shown by amphiphilic graft copolymers having a copolymer backbone but having a high degree of grafting (2G56, 2G58). Smid et al. [18] also observed the elution of associates of ABA triblock comb copolymers with oligo(oxyethylene) side chains in A blocks on GPC analysis in toluene. They put forward the hypothesis that an association phenomena was taking place in toluene. Evidently

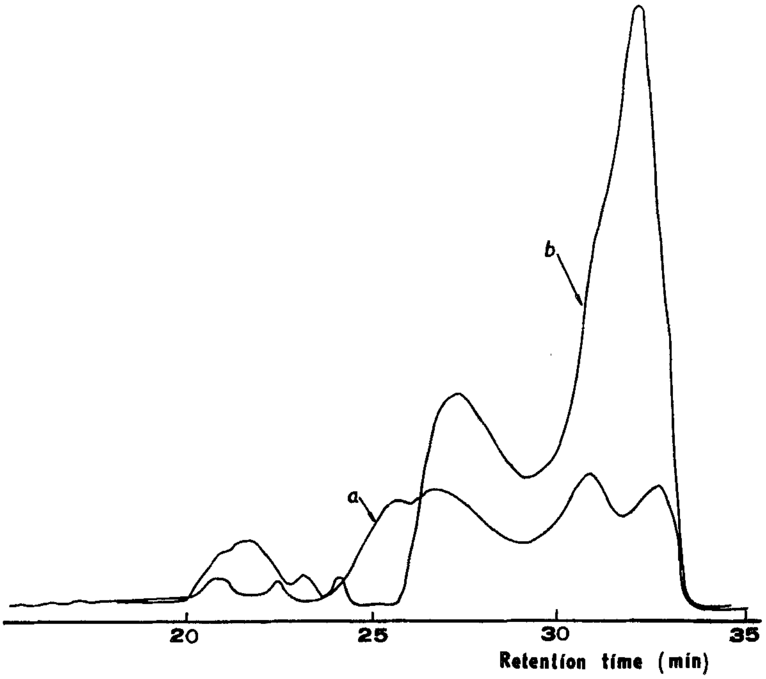


FIG. 1. GPC tracings of 1G50 in toluene at 90°C: (a) before complexation, (b) after complexation.

the intermolecular interactions of PEO side chains are favored when they are closely situated along the backbone. These observations are also in agreement with the results of Oiwa et al. [19] who stressed the importance of the physical interaction between PEO chains even in such a good solvent as benzene for the occurrence of crosslinking. On complexation with PhOK the hydrodynamic volume of the aggregated species decreased while that of the low molecular weight species remained unchanged (Fig. 1b).

Williamson Ether Synthesis

The Williamson ether synthesis was performed in the presence of the graft copolymers listed in Table 1. The backbone polymers did not exhibit any PTA, suggesting that PEO side chains impart catalytic activity to the graft copolymers. According to the widely assumed mechanism of phase-transfer catalysis by soluble PEOs [5, 11], dissolution of the salt in the organic phase is assisted by complexation of the cation by the ether oxygens in PEO. The observed pseudo-first-order kinetics implied that a constant amount of catalyst complex persisted during the reaction. Excess PhOK obviously provided pseudo-first-order conditions, and the linearity of the rate plots was maintained to high conversion.

The PTAs of the amphiphilic graft copolymers in the Williamson synthesis were evaluated at a constant concentration of ethereal oxygens and were compared with those of MPEO-NH_2 precursors. The results of these measurements, listed in Table 1, show the effects of the backbone structure, the graft density, and the length of the side chains on k_{obs}.

An important variable in the studies of the PTA of the graft copolymers was the graft density. Although the values of k_{obs} for a series of graft copolymers of constant length of the side chains differed within a factor of 2–4, the tendency of the catalytic activity to increase with an increase of the degree of grafting is obvious (Table 1). This effect is depicted in Fig. 2. In each series the copolymers with a low degree of grafting were less active than the parent MPEO-NH_2, while those with a high degree of grafting proved to be more active. In the series of graft copolymers with M_n(PEO) = 5000, only copolymers with a low degree of grafting were employed, and they yielded lower rates than did MPEO-5000-NH_2. An interesting result was obtained for the reaction carried out with the diblock copolymer poly(isoprene-*block*-PEO). Each block had a molecular weight of 5000. The value of k_{obs} for this copolymer was equal to that of MPEO-5000-NH_2. In this particular case the hydrophobic block did not affect the catalytic activity of the polyether block.

The results listed in Table 1 show that at an equal number of backbone units per PEO graft, the copolymers containing longer side chains were more active in the Williamson synthesis (2G52 and 2G74). These results agree with the tendency of a PEO's activity to increase with an increase of its molecular weight.

When PEOs are applied as PTCs, the reaction is promoted by activation of the bound ion pair. In solvents of low polarity this activation reflects the increase in the interionic ion pair distance [20]. When graft copolymers catalyze a phase-transfer reaction, there is a possibility of distribution of intra- and intergraft coordinations around the metal ion. The PTA of graft copolymers with a low degree of grafting is inferior to that of PEO homopolymers. The remote PEO chains may

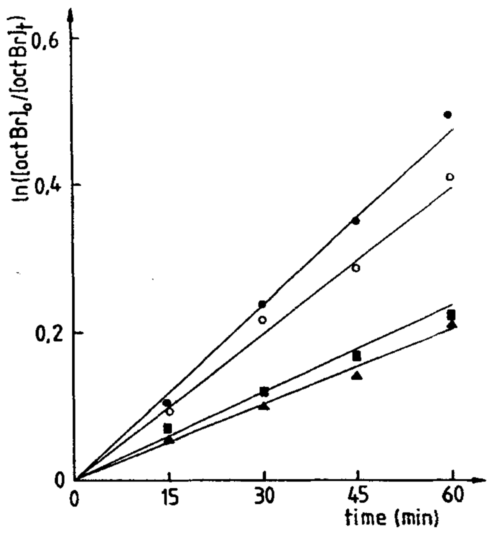


FIG. 2. Reaction of octylbromide (0.72 mmol) with PhOK (2.1 mmol) in toluene (3 mL) at reflux. Graft copolymer as catalyst (1.022 mmol oxygen): (●) 2G58, (○) MPEO-2000-NH_2, (■) 2G52, (▲) 2G55.

complex the ion pairs intramolecularly, and the effectiveness of this coordination increases with the length of the PEO chain [15]. At the junction points the rigidity of the PEO grafts increases, and this fact probably decreases their coordination ability compared to that of linear PEO of the same length. On the other hand, the steric hindrance of the backbone in the vicinity of the complexed PhOK might influence the reagent's contact and decrease the rate of the substitution reaction.

Intergraft coordinations around the metal ion are likely to occur with catalysts with a high degree of grafting. These polymers showed a propensity to aggregate in toluene even at 90°C. The strong cooperation of the intermolecular interactions is a reason to consider this phenomenon analogous to microphase separation. One can assume that in the particular case when graft copolymers with a high degree of grafting are applied as PTCs, the Williamson reaction proceeds in the PEO microphase where the enrichment and dissociation of PhOK ion pairs should be more favorable than in single PEO coils. The coordination of metal ions with the polyether phase might account for the decrease of the hydrodynamic volume of the aggregated species (Fig. 1).

The effect of the backbone structure was studied by determining the reaction rate constants in the presence of catalysts having a homopolymer backbone (series 1G47-50) or copolymer backbone (series 2G51-58). The following reasons might account for the lower catalytic activity of the graft copolymers derived from poly(PIA-*co*-St) (series 2G): 1) the copolymer backbone is less polar; and 2) with an equal extent of ester substitution, the PEO grafts in the copolymer derived from PPIA (series 1G) are separated by fewer monomer units, which favors their interchain interaction and hence the catalytic activity.

CONCLUSIONS

Amphiphilic graft copolymers consisting of a hydrophobic backbone and PEO side chains show phase-transfer activity under solid-liquid conditions. The catalytic activity of these copolymers in the reaction of potassium phenoxide with octylbromide in toluene depends on their degree of grafting, the length of the side chains, and the structure of the backbone. Only copolymers with a high degree of grafting are more active than the parent PEO. When there is an equal number of backbone monomer units between two grafts, the copolymer with longer grafts is more active.

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