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Ion Pair Affinities of Linear Polyethers Immobilized on Poly(styrene-*co*-*m*-TMI) Networks

Wen Ying Xu and Johannes Smid*

Polymer Research Institute, Faculty of Chemistry, College of Environmental Science and Forestry, State University of New York, Syracuse, New York 13210-2786

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ABSTRACT: Networks (RTMI) were synthesized by radical suspension polymerization of *m*-isopropenyl-α,α-dimethylbenzyl isocyanate (*m*-TMI), styrene, and divinylbenzene. They were then reacted with methoxypoly(ethylene glycol)s of molecular weights varying from 208 to 1900. The relative affinity of the immobilized polyethers for alkali metal ions in toluene was determined spectrophotometrically with alkali metal picrates (Pi^-M^+) by means of the competition equilibrium $Pi^-M^+N + L \rightleftarrows Pi^-M^+L + N$, where N is the RTMI-bound polyether and L is a ligand used to solubilize the picrate salt in toluene. For the same ligand L, the equilibrium constant *K* for a series of RTMI networks with different ligands N provides a measure of the relative binding constants of alkali metal picrates for the immobilized polyethers. The reliability of the competition method was checked, and the data were compared with the affinity of soluble polyethers for alkali metal picrates in toluene obtained by the same competition method but with different networks.

Introduction

In recent publications[1-10] we have demonstrated that network polymers with immobilized linear or macrocyclic polyethers are very useful in studying the formation of ligand complexes with ions and ion pairs, and in determining the affinity of ligands for ionic species in low polarity media. A competition-type method is employed in which an ionic chromophore, A^- (e.g., picrate or 8-anilinonaphthalenesulfonate), partitions itself between a network-immobilized ligand, N, and a soluble ligand, L, via complexation of its metal counterion, M^+ (reaction 1).

$$A^-M^+N + L \overset{K}{\rightleftharpoons} A^-M^+L + N \qquad (1)$$

By spectrophotometric measurement of the chromophore complex A^-M^+L (an ion pair in solvents such as dioxane, toluene, or chloroform), the equilibrium constant *K* can be determined. These K values provide a relative scale of binding affinities of soluble or immobilized ligands toward ionic species as a function of cation, anion, solvent, and temperature.[1-11] This information is very valuable when such ligands are used to catalyze ionic reactions or to modify the structure of reaction products.

In nearly all our investigations the ligand N was a linear or macrocyclic polyether immobilized on a microporous polystyrene resin. Cross-linked acrylate resins derived from methoxypoly(ethylene glycol) methacrylates have also been used,[5,12] and so have lightly cross-linked poly(ethylene oxide)s.[10,11] Hydroxyl- and amine-functionalized linear or macrocyclic polyethers can be effectively immobilized by reacting them with isocyanate containing networks. Such a resin can be obtained by copolymerizing *m*-isopropenyl-α,α-dimethylbenzyl isocyanate (*m*-TMI) and a vinyl monomer such as styrene. This unsaturated aliphatic isocyanate has been recognized as a very useful monomer in the synthesis of isocyanate-functionalized polymers.[13,14] We recently used *m*-TMI successfully to prepare well-defined polyfunctional isocyanates as precursors for star and network polymers.[15,16] This paper reports the synthesis and characterization of poly(styrene-*co*-*m*-TMI) networks and their reaction products with methoxypoly(ethylene glycol)s. Competition studies with a variety of soluble ligands using an alkali metal picrate as the chromophore are described and the data compared with those obtained for networks of different structures. The results confirm that the competition procedure with immobilized ligands constitutes a reliable method for establishing an affinity scale of ligands for ionic species.

Experimental Section

Materials. The monomer *m*-TMI, kindly provided by the American Cyanamid Co., was purified by vacuum distillation and the middle fraction collected for preparation of the network polymers. Methoxypoly(ethylene glycol)s (MPEG) of molecular weights 208, 350, 550, 750, and 1900 (Aldrich) were azeotroped with benzene. The first two then were vacuum distilled, while the last three were stripped of residual benzene under high vacuum. (Hydroxymethyl)benzo-18-crown-6 was available in our laboratory[3] and purified by twice recrystallization from diethyl ether. Tetra- and hexa(ethylene glycol dimethyl ether) (glyme 5 and glyme 7, respectively) were carefully distilled. Methoxypoly(ethylene glycol) monomethacrylate 400 (MG8) from Polysciences was azeotroped with benzene at low pressure. Propylene carbonate (PC) was distilled from CaH_2 under vacuum, while *N*-methylacetamide was used without purification. The preparation of picrate salts has been described.[3] The reaction product between *m*-TMI and MPEG750, abbreviated as TMI-750 (Scheme I), was prepared by reacting a slight excess of *m*-TMI with MPEG750 in a small amount of toluene for 16 h at 65 °C, using 1 wt % dibutyltin dilaurate (Aldrich) as catalyst. After treatment with carbon black in CH_2Cl_2, followed by filtration, solvent and excess *m*-TMI were removed under high vacuum at 80 °C, leaving a colorless product in 80% yield with no detectable NCO peak in the IR (2260 cm^{-1}). ^1H NMR ($CDCl_3$): δ 1.65 (s, 6, $(CH_3)_2C-$), 2.15 (s, 3, $CH_3C{=}C$), 3.3 (s, 3, OCH_3), 3.65 (64, OCH_2CH_2O), 4.0 (t, 2, $-CH_2OCO$), 5.0 (s, 1, NH), 5.25 (m, 2, $CH_2{=}$), 7.28 (m, 4, arom).

Network Preparation. In a typical example, a mixture of 3.5 g (17.4 mmol) of *m*-TMI, 5 g (48 mmol) of styrene, 0.6 g (4.6 mmol) of divinylbenzene, and 0.06 g (0.36 mmol) of azobis(isobutyronitrile) (AIBN) were added to 60 mL of water containing 1 wt % (based on monomers) of gelatin. The suspension was stirred vigorously at 70 °C for 20 h. After cooling, the resin (abbreviated as RTMI) was recovered by filtration, washed with acetone, and then extracted with THF in a soxhlet for 2 days to remove unreacted starting materials and other soluble residues. The yield of network after purification was about 60%. The IR spectrum revealed a strong NCO band at 2260 cm^{-1} but no urethane or amino absorptions. The NCO content of the resin was determined with excess dibutylamine in toluene and back-titration in 2-propanol with HCl and bromophenol blue as

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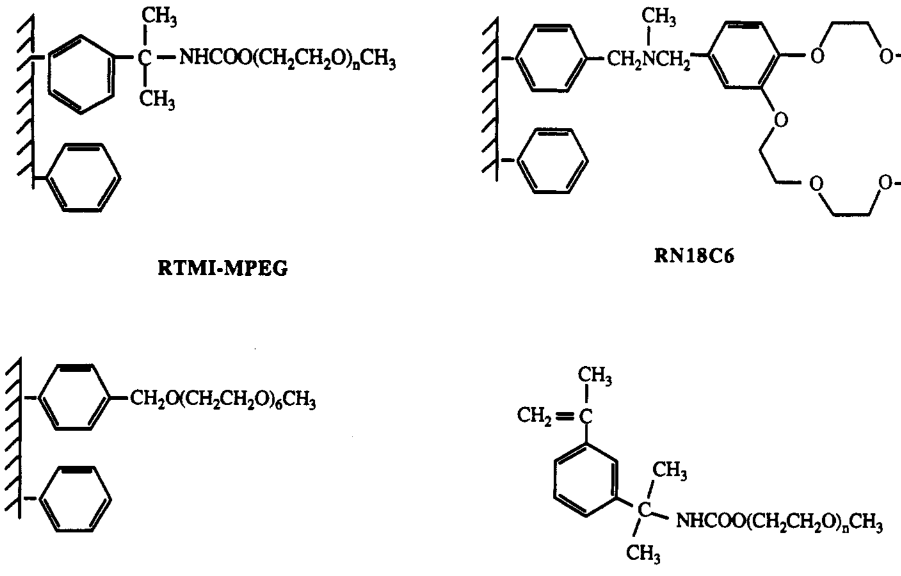
Scheme I



RTMI-MPEG

RN18C6

RG7I (0.61 mequiv/g)
RG7II (1.99 mequiv/g)

TMI-750 (n ~ 16)

indicator.[17] Residual NCO groups after 40-min reaction with the dibutylamine amounted to less than 2% (from IR).

Immobilization of Polyether Ligands. The general procedure was as follows. About 0.2–0.6 g of the RTMI resin was swollen in 3 mL of toluene, and excess MPEG was added, the molar ratio MPEG/NCO being approximately 5. About 1–2 vol % of dibutyltin dilaurate was added as catalyst (TMEDA was also an effective catalyst), and the mixture was heated with stirring at 85 °C for about 20 h. After cooling, the resin was recovered by filtration, washed with acetone, and then treated in a soxhlet with tetrahydrofuran for 24 h. After again washing with acetone, the resin was dried under vacuum at 30 °C. The IR spectrum showed no NCO absorption, but new bands appeared at 1700 cm^{-1} ($\nu_{C=O}$), at 3350 cm^{-1} (ν_{NH}) and in the 1050–1140-cm^{-1} region (ν_{C-O-C}). Titration with dibutylamine also did not reveal any residual NCO. A network containing bound benzo-18-crown-6 (RTMI–B18C6) was made in a similar way using (hydroxymethyl)benzo-18-crown-6.

Measurements. The competition method for determining the equilibrium constant of the reaction $A^-M^+N + L \rightleftarrows A^-M^+L + N$ (K) has been described.[2,4] Briefly, a known quantity of picrate salt is dissolved in 10 mL of toluene by means of a minimum amount of a ligand, L. The total $[Pi^-M^+L]_0$ is on the order of 10^{-4} M. A quantity of a resin with the immobilized ligand N (from 2 to 15 mg), sufficient to transfer most of the picrate salt to the network, is then introduced to the solution. After equilibrium is established (about 40 min), known amounts of ligand L are added. After each addition, and upon reaching equilibrium, the concentration of Pi^-M^+L is measured spectrophotometrically in an optical cell attached to the apparatus (λ_m = 330–360 nm, depending on counterion and ligand; see ref 4). The amount of resin-bound salt (Pi^-M^+N, in mequiv) is calculated from $[Pi^-M^+N] = [Pi^-M^+L]_0 - [Pi^-M^+L]$.

Results and Discussion

While m-TMI homopolymerizes at low temperature by cationic initiators,[13] no polymer is formed with radical initiators such as benzoyl peroxide or AIBN. However, it easily copolymerizes with vinyl monomers such acrylates and styrene. At least 50 mol % m-TMI can be incorporated into the copolymer, the reactivity ratios for the monomer pair m-TMI (M_1)–styrene (M_2) being $r_1 = 0.72$ and $r_2 = 0.80$.[13] The isopropyl group adjacent to the isocyanate function renders the NCO moiety less sensitive to water. As a result, radical polymerization with m-TMI can be carried out in a suspension or emulsion without affecting the NCO group as long as the temperature is not too high.[13] Our network with m-TMI, styrene, and divinylbenzene made in an aqueous suspension did not possess an NH band in the infrared, as would be expected if NCO had reacted with water. The amount of m-TMI in the network was kept between 3 and 6.5 wt % NCO, that is, between 0.7 and 1.6 mequiv of NCO groups/g of RTMI resin. This amounts to about one m-TMI unit per seven to fifteen styrene units.

The reaction of RTMI with MPEG or (hydroxymethyl)benzo-18-crown-6 in the presence of the tin catalyst proceeds smoothly and goes to completion as long as the temperature is kept around 80 °C. No residual NCO was found in the infrared (the general structure of the RTMI–MPEG networks is shown in Scheme I). Calculation of the equilibrium constant K requires a knowledge of the amount of ligand N in the resin. The benzo-18-crown-6 content can easily be obtained by swelling the resin in dioxane to which is added a sufficient amount of potassium picrate to saturate the resin with Pi^-K^+. The residual picrate salt in the solution is then measured spectrophotometrically.[3] Since a 1:1 complex is formed, saturation by Pi^-K^+ yields the crown content. For the linear polyethers the binding with alkali metal ions is much weaker, and saturation is more difficult to achieve. Moreover, ligands such as MPEG750 or -1900 can accommodate more than one Pi^-K^+ ion pair. Therefore, we have assumed that the reaction of MPEG with RTMI is quantitative and that the MPEG content equals the amount of NCO found by titration with dibutylamine.

Determination of Equilibrium Constants and Reliability of the Method. The constant K of reaction 1 can be obtained from the expression

$$(1/F_2) - 1 = K[(1/F_1) - 1] \qquad (2)$$

where F_2 is the fraction of RTMI-bound ligand N complexed to Pi^-K^+ ion pairs, i.e., $F_2 = Pi^-M^+N/N_0$, N_0 being the ligand content (in mequiv/g) of the network.[2,4] F_1 denotes the fraction of soluble ligand, L, bound to Pi^-M^+, i.e., $F_1 = Pi^-M^+L/L_0$, where L_0 is the initial concentration of L. It is assumed that N and L only form 1:1 complexes with the picrate salt, although as stated earlier a ligand such as MPEG1900 with more than 40 ethylene oxide units can bind in principal more than one ion pair. However, this is not likely to occur in our system since experimental

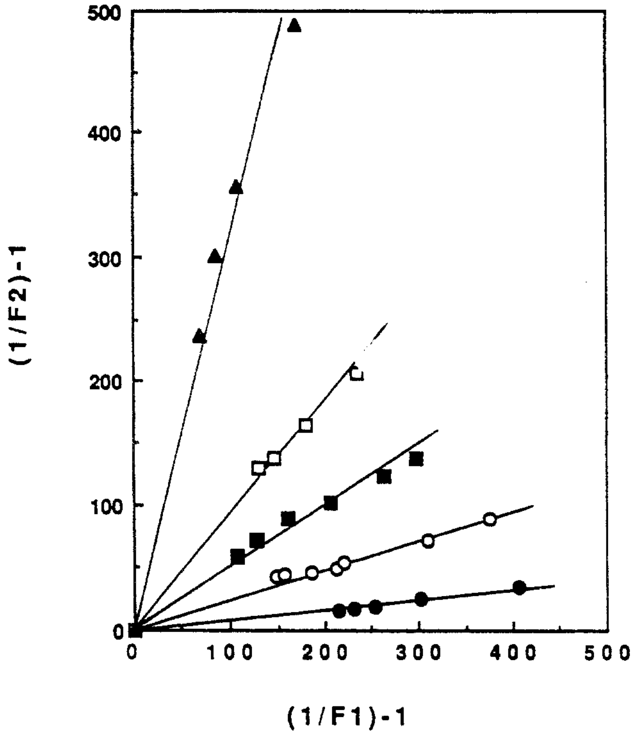


Figure 1. Plots of $(1/F_2) - 1$ vs $(1/F_1 - 1)$ for the reaction $Pi^-K^+N + G7 \rightleftarrows Pi^-K^+G7 + N$ in toluene at 25 °C. N is the network RTMI on which a linear polyether MPEG is immobilized. The molecular weights of the MPEG chains are 1900 (●), 750 (○), 550 (1.45 mequiv/g) (■), 350 (□), and 208 (▲). (See also Table I.)

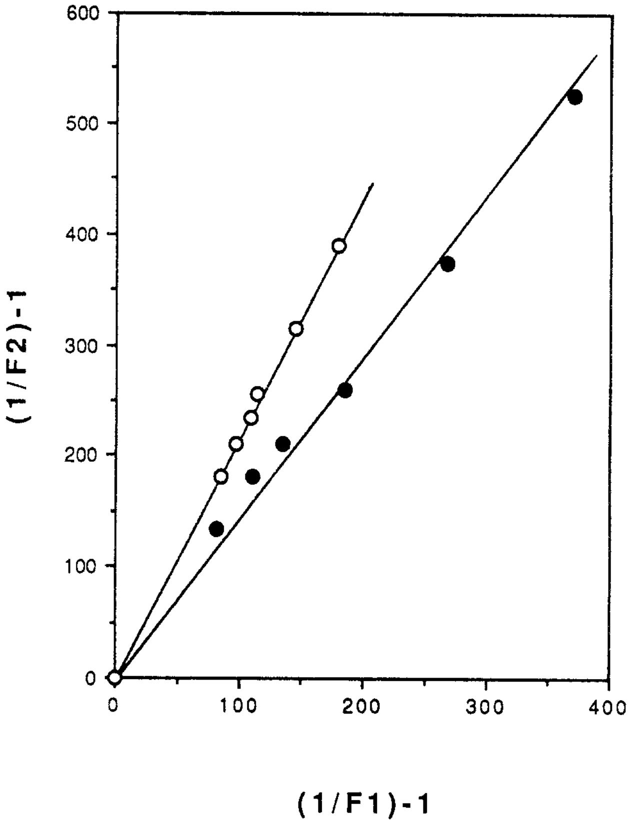


Figure 2. Plots of $(1/F_2) - 1$ vs $(1/F_1) - 1$ for the reaction $Pi^-K^+N + G7 \rightleftarrows Pi^-K^+G7 + N$ in toluene at 25 °C, where N is the network RG7I (○) or RG7II (●).

Table I. Equilibrium Constants, K, of the Reaction $Pi^-K^+N + G7 \rightleftarrows Pi^-K^+G7 + N$ in Toluene at 25 °C for Network Polymers with Different Immobilized Ligands N[a]

network[b] (mequiv/g)	wt %[c] ligand	EO units[d] per ligand	K	K(RTMI-208)/K
RN18C6 (0.65)	20		0.0070	457
RTMI–B18C6 (1.35)	32		0.0092	348
RTMI–1900 (1.38)	72	42.5	0.078	41.0
RTMI–750 (1.42)	50	15.2	0.22	14.5
RTMI–550I (0.81)	30	11.3	0.55	5.8
RTMI–550II (1.45)	43	11.3	0.48	6.6
RTMI–350 (1.50)	34	7.1	0.92	3.5
RTMI–350A (1.50)	34	7.1	1.0	3.2
RTMI–208 (1.50)	24	4	3.2	1.0
RG7I (0.61)	19	6	2.2	1.45
RG7II (1.99)	61	6	1.44	2.2

[a] G7 is glyme 7 or hexa(ethylene glycol dimethyl ether). [b] RN18C6, RG7I, and RG7II are microporous polystyrene networks with immobilized benzo-18-crown-6[7] and glyme 7 ligands,[4]; respectively. For the RTMI networks, the number in brackets refers to the original NCO content of each resin in milliequivalents per gram of network, while for RN18C6 and the two RG7 resins it denotes the ligand content in these resins. Network RTMI–350A differs from RTMI–350 in that the terminal OH group in MPEG was replaced by NH_2. [c] The wt % of ligand in the RTMI networks was calculated on the assumption that all NCO groups had reacted with the added ligand. [d] Average number of ethylene oxide units, based on the molecular weights of the MPEG as determined by ^1H NMR (see text and ref 18).

conditions are such that the concentrations of N and L are larger than that of the picrate salt by at least a factor 10 (e.g., note the values of $1/F_2 - 1$ and $1/F_1 - 1$ in Figures 1 and 2).

Most experiments were carried out with potassium picrate in toluene at 25 °C. Figure 1 depicts plots of $(1/F_2) - 1$ vs $(1/F_1) - 1$ for five competition equilibria. The soluble ligand L is glyme 7 (hexa(ethylene glycol dimethyl ether), the number 7 referring to the number of available oxygen binding sites) while N is a RTMI-bound MPEG ligand of molecular weight (MW) varying from 208 to 1900. K values, which equal the slope of the linear plots, are collected in Table I. Included in this table are data for RTMI–B18C6 and RN18C6, two benzo-18-crown-6 containing networks, and for RG7I and RG7II, networks with the ligand $CH_3O(CH_2CH_2O)_6CH_2$ anchored to a benzene ring (see Scheme I for structures). RG7I and II are microporous polystyrene resins previously used with lithium and sodium picrate in toluene,[4] while RN18C6 was used to obtain K values for the potassium salt in dioxane and tetrahydrofuran.[7]

In our earlier studies only a few networks were employed while the structure of L was varied. In the present work the chief objective was to vary the network-bound ligand. It can easily be verified that

$$K = K_L/K_N \qquad (3)$$

where K_L is the formation constant of the Pi^-M^+L complex ($Pi^-M^+ + L \rightleftarrows Pi^-M^+L$) and K_N is the binding constant of Pi^-M^+ to the immobilized ligand N. K_N has been determined independently for a number of crown ether containing networks and alkali metal picrates and with anilinonaphthalenesulfonate salts in ether-type solvents, e.g., dioxane and tetrahydrofuran.[2,3,6,7] Coupled with K values measured for a series of soluble ligands with the same network/salt/solvent combination, the K_L for these ligands can then be computed from eq 3. Unfortunately, the insolubility of picrate salts in toluene prevents the direct measurement of K_N in this solvent. Neverthless, for a series of networks and the same soluble ligand L, e.g., glyme 7, K values such as those listed in Table I provide us with a relative scale of the binding affinities of these networks for Pi^-K^+ in toluene. It permits us to interpret differences in K values in terms of changes in network structure or in the nature or content of the bound ligand.

Table II. Comparison of the Binding of Potassium Picrate with Different TMI–Glyme Networks in Toluene at 25 °C

network	ligand	K	ratio of K's
RTMI–1900	G7	0.078	0.355
RTMI–750	G7	0.22	
RTMI–1900	TMI–750	0.53	0.353
RTMI–750	TMI–750	1.50	
RTMI–1900	D4TMI–750	0.55	0.324
RTMI–750	D4TMI–750	1.70	
RTMI–1900	TMI–750	0.53	6.79
RTMI–1900	G7	0.078	
RTMI–750	TMI–750	1.5	6.82
RTMI–750	G7	0.22	
RTMI–550I	G7	0.55	2.04
RTMI–550I	G5	0.27	

The reliability of the competition method can be checked by comparing the ratio of K values obtained for two networks A and B and the same ligand L with the ratio of K values determined for the same two networks but with a different soluble ligand. For the two networks A and B and the soluble ligand L the respective relationships $K(\mathrm{A}) = K_\mathrm{L}/K_\mathrm{N}(\mathrm{A})$ and $K(\mathrm{B}) = K_\mathrm{L}/K_\mathrm{N}(\mathrm{B})$ can be written. The ratio of the two K values equals $K(\mathrm{A})/K(\mathrm{B}) = K_\mathrm{N}(\mathrm{B})/K_\mathrm{N}(\mathrm{A})$ and is independent of the soluble ligand used in determining $K(\mathrm{A})$ and $K(\mathrm{B})$. In Table II ratios of K values obtained for the networks RTMI–1900 and RTMI–750 with three different ligands L are given. The average value of $K(\mathrm{A})/K(\mathrm{B})$ equals 0.344 ± 0.013, or $K_\mathrm{N}(\text{RTMI–1900})/K_\mathrm{N}(\text{RTMI–750}) = 2.91 \pm 0.11$. Alternatively, the ratio of two K values measured for two ligands L_1 and L_2 with the same network should be independent of the chosen network, and $K(1)/K(2) = K_\mathrm{L}(1)/K_\mathrm{L}(2)$. This is demonstrated in Table II for the ligands glyme 7 and TMI–750 (Scheme I), using the two networks RTMI–1900 and RTMI–750. The respective ratios $K(1)/K(2)$ or $K_\mathrm{L}(1)/K_\mathrm{L}(2)$ are 6.82 and 6.79. The two sets of data demonstrate that the competition method with the RTMI networks yields reliable information on ion pair interactions with both soluble and immobilized ligands, a conclusion reached earlier for RG7I and for crown containing resins.[4,7]

Network Affinities for Ion Pairs. The last column of Table I lists the ratio $K(\text{RTMI–208})/K$. This ratio equals $K_\mathrm{N}/K_\mathrm{N}(\text{RTMI–208})$, which represents the binding constant of $\mathrm{Pi^-K^+}$ to a network relative to its binding constant to RTMI–208. The latter has a bound polyether with an average of 4 ethylene oxide (EO) units. The number of EO units for other RTMI-bound polyether ligands is listed in column 3 of Table I. They were derived from the MW of the respective ligands, as determined recently by ^{1}H NMR.[18] The corrected MW's for MPEG-350, -550, -750, and -1900 were found to be 345, 530, 700, and 1900, respectively.

The increase in the relative affinity of immobilized MPEG for $\mathrm{Pi^-K^+}$ as a function of the MW or number of EO units of the polyether parallels that found for soluble glymes with lithium and sodium picrate in toluene.[4] Gokel *et al.*[19] reported a linear correlation between the binding constant of poly(ethylene glycol)s (PEG) to the free sodium ion in methanol and the MW of PEG for MW >500. Insufficient data in this MW range prevents us from checking this relationship for our RTMI-bound MPEG's. However, the K values found for RTMI-750, and RTMI-1900 suggest a proportionality with the number of EO units. The shorter MPEG ligands deviate from the correlation and appear to be less efficient in their binding than expected. This may be caused by steric interference between the bound picrate ion pair and the polymer chain with its bulky TMI unit when the binding site is close to the chain. It resembles the observation that increasing the spacer length of polymer-bound ligands generally improves their effectiveness to complex cations.[3] It also was found to enhance the anion-activating effect of crown ether networks in phase transfer catalysis.[20]

Proximity to the bulky polymer chain is at least in part responsible for the lower ion pair binding constant of immobilized polyethers relative to that of a free polyether of the same structure. For example, the K for the combination RTMI–750/TMI–750 equals 1.5, and K equals 2.2 for RG7I/G7 (Table I). In addition to diminished accessibility a polymer-bound polyether may also be less flexible than the free ligand. It would make it more difficult for the former to assume a conformation that is optimal for effective complexation of the ion pair.

A higher ligand content of the network apparently increases its ion pair binding constant. For example, compare RTMI–550I with RTMI-550II and RG7I with RG7II (Table I). This agrees with similar observations for crown ether containing networks.[3] The higher capacity networks have a more polar microenvironment for the ion pair which should favor its binding. Also, the cation may complex simultaneously with two bound polyethers. Such a cooperative effect should be more pronounced in a network with high ligand content. This effect is especially important when 2:1 ligand–cation complexes are prevalent.[7]

The higher binding constant of $\mathrm{Pi^-K^+}$ for RN18C6 as compared to RTMI–B18C6 (both have the same benzo-18-crown-6 ligand) may be caused chiefly by a substituent effect in addition to the bulkiness of the *m*-TMI units in RTMI resins. The $\mathrm{RNHCOOCH_2}$ substituent of B18C6 in the latter network has a higher σ value than the $\mathrm{RCH_2(CH_3)NCH_2}$ group in RN18C6. Such differences in Hammett σ constants have a significant effect on the binding constants of cations to substituted benzo crown ethers.[21] Another point to note is that TMI–750 and D4TMI–750 have nearly the same K values. The latter compound is a four-armed star polymer[18,22] with MPEG arms obtained by reacting MPEG750 with the tetraisocyanate D4TMI, a hydrosilylation product of *m*-TMI and tetramethylcyclotetrasiloxane.[16] This K value was measured to determine the presence of any cooperative effect of the arms on complexing $\mathrm{Pi^-K^+}$. Apparently, this does not occur.

A few experiments were carried out with lithium picrate in order to compare the chelating ability of linear polyethers (glymes) with that of propylene carbonate (PC) and *N*-methylacetamide (NMA). The two polar compounds have been used in our recent work with gel polymer electrolytes composed of poly(ethylene oxide) networks containing lithium salts.[23,24] The high dielectric constants of these additives promote ion pair dissociation, but ^{13}C NMR data reveal that in mixtures of glyme 5, PC, and $\mathrm{LiClO_4}$ the lithium ions remain predominantly bound to the glyme even up to 90 mol % PC.[25] To independently check the chelating ability of these compounds with lithium salts, K values were determined with the network RTMI–1900 and lithium picrate in toluene. In addition to PC and NMA, methoxypoly(ethylene glycol) methacrylate (MG8) having an average of eight ethylene oxide units was also used as a soluble ligand. The K values were found to be 0.00016 (PC), 0.0035 (NMA), and 0.2 (MG8). However, those for PC and NMA increase at higher ligand concentrations, implying the formation of complexes of $\mathrm{Pi^-Li^+}$ with more than one PC or NMA molecule. Nevertheless, the chelating ability of PC or NMA with $\mathrm{Li^+}$ ions relative to that of a glyme such as MG8 is poor in spite of their highly polar character, confirming our findings from ^{13}C NMR measurements. With the network RG7I and Pi$^-$Li$^+$, the compound NMA yielded $K = 0.039$, comparable to the values 0.027 and 0.028 reported for tetramethylethylenediamine and glyme 3, but still 50 times below that of glyme 5.[4]

Finally, the optical absorption maxima of the picrate salt–ligand complexes imply that in toluene the ionic species are present in the form of polyether complexed tight ion pairs. For example, the λ_m of complexes of glyme 5, 6, or 7 with the picrate salts are found at 346 (Li), 350 (Na), and 357 (K) nm. These values are typical for that of tight picrate ion pairs.[4] The λ_m of a ligand-complexed separated picrate ion pair such as the complex of Pi$^-$K$^+$ with a bis(crown ether) in tetrahydrofuran is found at 380 nm.[26]

In conclusion, the results demonstrate that the competition method yields reliable information on the affinities of free and network-bound linear polyethers and other ligands for ionic species in low polarity solvents. From an experimental point of view, data acquisition is facilitated when the affinities of the immobilized and free ligands are not too far apart. A network which strongly binds the ionic chromophore requires a large amount of a weak-binding soluble ligand to release the chromophore into the solution. This in turn will change the properties of the medium and makes it more difficult to interpret the data. For this reason, the availability of a series of networks in which the binding strength of the bound ligand varies over a wide range is important. It makes it possible to study the interaction between a soluble ligand and the ionic species over a wide range of ligand concentrations. This is especially important when complexes of different stoichiometries can exist.

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References and Notes

(1) Smid, J.; Sinta, R. *Top. Curr. Chem.* **1984**, *121*, 105.

(2) Sinta, R.; Rose, P. S.; Smid, J. *J. Am. Chem. Soc.* **1983**, *105*, 4337.

(3) Sinta, R.; Lamb, B.; Smid, J. *Macromolecules* **1983**, *16*, 1382.

(4) Xu, W. Y.; Smid, J. *J. Am. Chem. Soc.* **1984**, *106*, 3790.

(5) Xu, W. Y.; Smid, J. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 173.

(6) Wakui, T.; Smid, J. *J. Inclusion Phenom.* **1985**, *3*, 197.

(7) Xu, W. Y.; Roland, B.; Smid, J. *Macromolecules* **1985**, *18*, 2061.

(8) Wakui, T.; Smid, J. *J. Phys. Chem.* **1986**, *90*, 4618.

(9) Buese, M. A.; Hogen Esch, T. E.; Xu, W. Y.; Smid, J. *Makromol. Chem.* **1987**, *188*, 1631.

(10) Tsvetanov, Ch. B.; Petrova, E. B.; Dimov, D. K.; Panayotov, I. M.; Smid, J. *J. Solution Chem.* **1990**, *19*, 425.

(11) Dimov, D. K.; Petrova, E. B.; Panayotov, I. M.; Tsvetanov, Ch. B. *Macromolecules* **1988**, *21*, 2733.

(12) Wakui, T.; Xu, W. Y.; Chen, C. S.; Smid, J. *Makromol. Chem.* **1986**, *187*, 533.

(13) Dexter, R. W.; Saxon, R.; Fiori, D. E. *J. Coat. Technol.* **1986**, *58*, 43.

(14) Arent, V. D.; Logan, R. E.; Saxon, R. *J. Cellular Plast.* **1982**, 376.

(15) Zhou, G. B.; Fragnito, R.; Smid, J. *J. Polym. Bull.* **1989**, *22*, 85.

(16) Zhou, G. B.; Smid, J. *J. Polym. Sci. Polym. Chem. Ed.* **1991**, *29*, 1097.

(17) Furukawa, M.; Yokoyamata, T. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 175.

(18) Zhou, G. B. Ph.D. Thesis, State University of New York, Syracuse, NY, September, 1992, p 134.

(19) Gokel, G. W.; Goli, D. M.; Schultz, R. A. *J. Org. Chem.* **1983**, *48*, 2837.

(20) Molinari, H.; Montanari, F. *J. Chem. Soc., Chem. Commun.* **1977**, 639.

(21) Ungaro, R.; El Haj, B.; Smid, J. *J. Am. Chem. Soc.* **1976**, *98*, 5198.

(22) Zhou, G. B.; Smid, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *31* (2), 613.

(23) Xia, D. W.; Sein, A.; Smid, J. In *Contemporary Topics in Polymer Science*; Salamone, J. C., Riffle, J., Eds.; Plenum Press: New York, 1992; Vol. 7, p 229.

(24) Xu, W. Y.; VanBeylen, M.; Smid, J. *J. Solid State Ionics* **1992**, *52*, 133.

(25) Fish, D.; Smid, J. *Electrochim. Acta* **1992**, *37*, 2043.

(26) Bourgoin, M.; Wong, K. H.; Hui, J. Y.; Smid, J. *J. Am. Chem. Soc.* **1975**, *97*, 3462.