Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Yamashita, Yuya and Tsukahara, Yasuhisa(1984) 'Synthesis and Application of Tailored Graft Copolymers from Polystyrene Macromonomer', Journal of Macromolecular Science, Part A, 21: 8, 997 — 1012
To link to this Article: DOI: 10.1080/00222338408056587
URL: http://dx.doi.org/10.1080/00222338408056587

J. MACROMOL. SCI.—CHEM., A21(8&9), pp. 997-1012 (1984)

Synthesis and Application of Tailored Graft Copolymers from Polystyrene Macromonomer

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SUMMARY

Comb graft copolymers prepared by macromonomer technique has become applicable for permanent modification of polymer surfaces. In this paper the association and adsorption behavior in solution of the well designed graft copolymer prepared from polystyrene macromonomer and various hydrophilic comonomer was studied and the mechanism of surface accumulation of hydrophilic segment was clarified by surface analysis of polystyrene containing the graft copolymers. Wetting of modified polymer surfaces and the permeability of gases through the film was also discussed.

INTRODUCTION

Surface structure and properties of high polymers are known to be of considerable importance in determining their applications for uses as coatings, adhesives, films, fibers and moldings. We proposed a new surface modification techniques consisting of blending comb graft copolymers in polymer matrix to obtain a controlled

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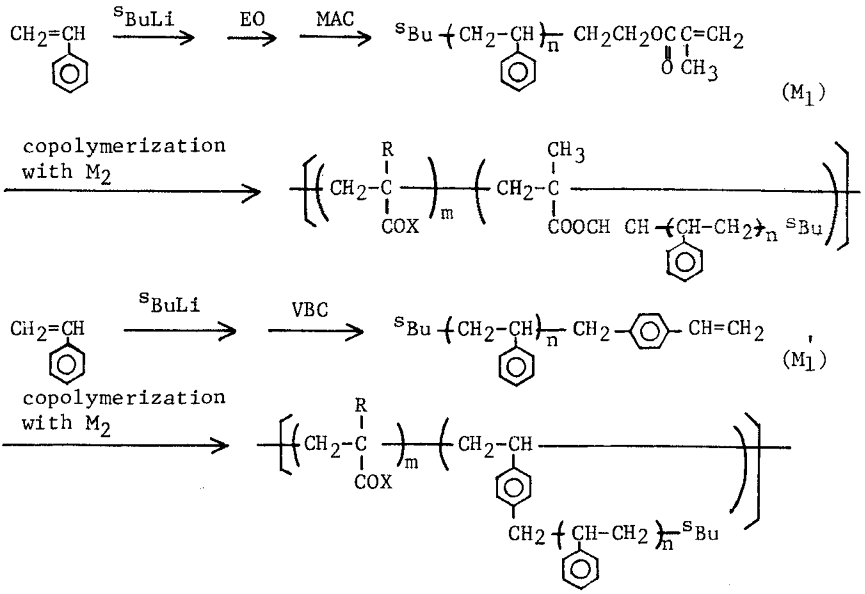
surface structure for any particular application.[1,2) Comb graft copolymers of well defined structure has become available by the copolymerization of the macromonomer with various functional comonomers. In polymer matrix, the functional comonomer segment (may be hydrophobic or hydrophilic) can been accumulated on the surface induced by environmental conditions and stabilized by the anchor segment compatible with the matrix polymers. Permanent modification of conventional polymers by using preformed graft copolymers is useful for various application. Hydrophobic modification of polar polymers is useful to improve water and oil repellency, and frictional properties. Hydrophilic modification of nonpolar polymers is useful to improve adhesion, wetting, coating and antistatic properties. This paper presents some basic studies on the surface activity of the hydrophilic graft copolymers prepared from polystyrene macromonomer.

EXPERIMENTAL

Materials

Graft copolymers were prepared according to Scheme 1. PSt macromonomer (M_1) was obtained by the method of Milkovich[3)], using a high-vacuum technique. Styrene was polymerized in benzene by sec BuLi, endcapped by ethylene oxide (EO) and deactivated by methacryloyl chloride (MAC). The macromonomer was precipitated by methanol. Yield was quantitative and molecular weight was close to the calculated value, and the molecular weight distribution was sharp with M_w/M_n around 1.1. The terminal methacrylate double bond can be analyzed by NMR and bromine titration to the accuracy of



Scheme 1 Preparation of graft copolymers

above 90% purity. In some cases, macromonomer with terminal styrene group was prepared by endcapping of living PSt with p-vinylbenzyl chloride (VBC).

Radical copolymerization of the PSt macromonomers with hydrophilic comonomers was carried out to high conversion at 60°C in an ampoule by using DMF or THF as an solvent and α,α'-azobisisobutyronitrile (AIBN) as an initiator. The graft copolymers were precipitated out of methanol or water, reprecipitated from THF into methanol or diethyl ether. Unreacted macromonomers were removed by extraction with diethyl ether or cyclohexane. Trace amounts of homopolymers consisting of comonomers were removed by methanol. The graft copolymers thus obtained were confirmed to be satisfactorily pure by the single peak in GPC. The graft copolymers were

Table I. Characterization of Graft Copolymers

		Composition (wt%)a)				$\overline{M}_n x10^{-3}$ b)	
Sample	Type	Comonomer		MMA	PSt	Branch	Total
GAS-1	G (MAA/MMA-PSt)	MAA	28.9	34.8	36.3	9.7	58.6
GAS-2	G (MAA/MMA-PSt)	MAA	35.3	18.9	45.8	9.7	55.0
GAS-3	G (MAA/MMA-PSt)	MAA	55.4	3.7	40.9	9.8	50.6
GHS-1	H (HEMA-PSt)	HEMA	28.0	-	72.0	4.0	28.8
GHS-2	G (HEMA-PSt)	HEMA	56.0	-	44.0	4.0	24.9
GHS-3	G (HEMA-PSt)	HEMA	85.0	-	15.0	4.0	27.0
GHS-4	G (HEMA-PSt)	HEMA	61.0	-	39.0	11.3	80.2
GSS-1	G (AMPS/MMA-PSt)	AMPS	49.0	-	51.0	13.2	29.3

a) calculated by elemental analysis and ^{1}H-NMR
b) determined by GPC using PSt and PEO calibration curve
c) MAA=methacrylic acid, HEMA=2-hydroxyethyl methacrylate
AMPS=2-acrylamido-2-methyl-propanesulfonic acid

characterized by ^{1}H NMR, IR, elemental analysis and GPC. The results are summarized in Table I.

Methods

PSt film specimens containing various amounts of the graft copolymers were cast into thin films of about 0.1 mm thickness by pouring dilute solutions of 5 w/v % concentration in THF onto clean glass slides and evaporating the solvent gradually at about 30°C, dried under vacuum. To obtain clear solution, MeOH is added sometimes.

Contact angle of water droplet was measured at 20°C with goniometer. IR spectra was measured on KRS prism by ATR method using FT-IR instrument. XPS spectra was measured at 10^{-7} torr.

Permeability of gases was measured at 25°C by a Rouse type apparatus. Pressure difference was controlled by saturated vapor pressure and liquid nitrogen trap. Permeability coefficient P $ccstp\cdot cm^{-1}\cdot s^{-1}\cdot cmHg^{-1}$ was calculated from $P=q_s l/p$, where q_s stands for rate of mass flux, l film thickness, p pressure difference.

RESULTS AND DISCUSSION

Synthesis of the graft copolymers

Graft copolymers were prepared according to Scheme 1 with the results summarized in Table I. Molecular weights and distributions were estimated by GPC, which accounts for roughly from one to six PSt branches per molecule. Estimated molecular weight from GPC by using PSt calibration curve is expected to show lower values for comb graft copolymers and some samples were corrected by the molecular weight from membrane osmometer, which showed 30-50% higher value. The molecular weight of the graft copolymer was shown to depend on the monomer concentration and the initiator concentration during the copolymerization. The purity or the composition distribution of the graft copolymer depends on the monomer reactivity in the copolymerization. The macromonomers and the comonomers were all chosen from acrylate or styrene type to keep the composition distribution not too broad even at high conversions. In the present experiment the copolymerization was expected to proceed in an ideal behavior in a homogeneous solution[4,5].

Micelle formation of the graft copolymer in solution

Amphiphilic graft copolymers are expected to form micellar aggregates in a particular solvent above critical micelle concentration. This can be observed by the broadening of NMR peaks in solution due to the restricted motion of the segments.[5] In ^1H NMR spectrum of St-HEMA random copolymer, peaks due to the PSt segments appeared at δ 6.5-7.0 (C_6H_5) and peaks due to the PHEMA segments appeared at δ 3.7-4.1 (OCH_2CH_2O) as observed in Figure 1 (a). Figure 1 (b) shows the spectrum of PSt rich graft copolymer (GHS-1), which is apparently soluble in $CDCl_3$ to give a clear solution, but the spectrum shows only those peaks due to PSt segments. With the addition of CD_3OD, the peaks due to PHEMA segments also appeared. This clearly indicates that the PHEMA segments insoluble in chloroform constitute a micelle core which behaves as a solid on the NMR time scale, consequently their peaks are too broad to be observed. On the other hand, PSt segments are molecularly dispersed in

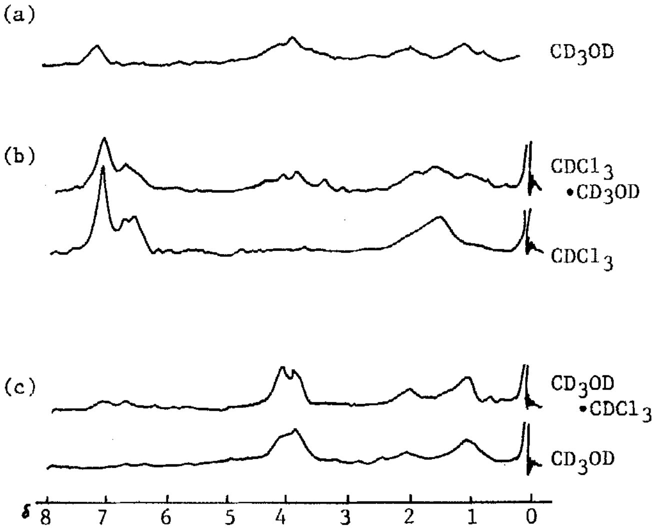


Figure 1. ^1H NMR spectra of St-HEMA copolymers

(a) random copolymer in CD_3OD
(b) graft copolymer (GHS-1) in $CDCl_3$, and in $CDCl_3$-CD_3OD (20 vol%)
(c) graft copolymer (GHS-3) in CD_3OD, and in CD_3OD-$CDCl_3$ (20 vol%)

chloroform to show well resolved NMR peaks. Methanol is a good solvent for PHEMA segments and destroys the micelle structure to show normal spectrum in the mixed solvent. The reverse phenomenon is observed with a PHEMA rich graft copolymer (GHS-3), which showed only those peaks due to PHEMA segments in CD_3OD, indicating the formation of a micelle of PSt core surrounded by PHEMA segments. Addition of $CDCl_3$ destroys the micelle to give a normal spectrum in Figure 1 (c).

The surface properties of cast films reflect the micelle structure in solution. Contact angle of water droplet on polymer films cast from appropriate solvents were measured at 20°C to estimate the surface structure. Random copolymers of St-HEMA showed, as expected, a smooth change in cos θ with composition, becoming more wettable with increasing HEMA (hydrophilic) content, independent of the cast solvent as shown in Figure 2 (a). The graft copolymers showed very interesting wetting properties as shown in Figure 2 (b). When cast from DMF, a good solvent for both homopolymers, their contact angles were very close to that of PSt and independent of composition, even with a sample of 85 wt% HEMA (GHS-3). It is reasonable to consider that the PSt domains with lower surface energy would dominate on the polymer surface different from the bulk composition. This sample, however, was significantly more wettable when cast from methanol. This results clearly suggest that the surface properties of graft copolymers are also controlled by microphase separation phenomenon. Thus, the polymer cast from methanol, a selective solvent for PHEMA,

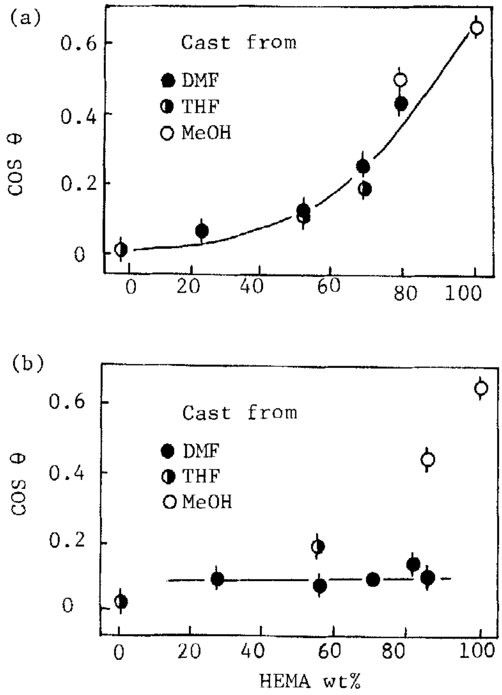


Figure 2. Contact angles of water on St-HEMA copolymer films.
(a) random copolymer (b) graft copolymer

appears to retain its structure as in solution, i.e., with a PSt core covered with PHEMA.

Surface accumulation of the graft copolymer in polymer solids

The results of the wettability variations of PSt films with added graft copolymer concentration are shown in Figure 3. For the comparison of hydrophilic segments to obtain polar surface, advancing contact angle on glass side surface is shown. Contact angle on air side surface has an almost constant value of 90° similar to PSt surface. On the other hand, glass side surface become

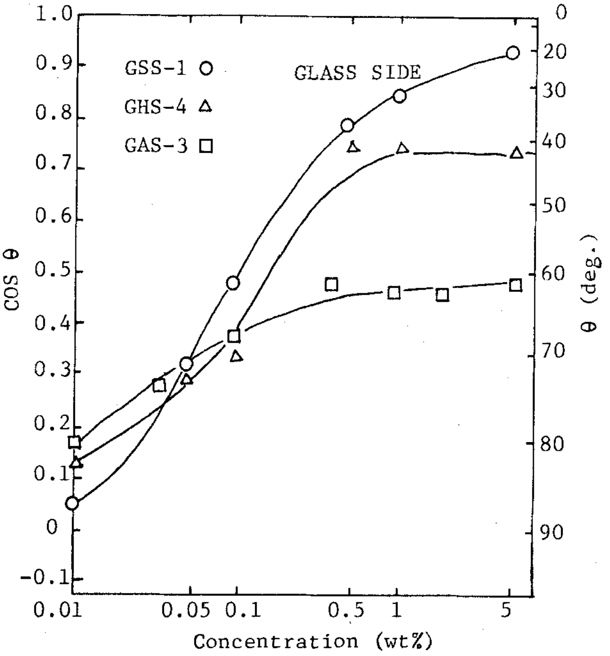


Figure 3. Contact angle variations for water on PSt film specimens containing graft copolymers

wettable by adding small amount of the hydrophilic graft copolymer. The change of contact angle is marked near the concentration of 0.1 wt%. The order of effectiveness follows sulfonic acid group > carboxylic acid group > hydroxyl group, which is the usual order of hydrophilicity. Contact angle below 30° is attained by using below 1% of sulfonic acid containing graft copolymer.

The mechanism of surface accumulation of the graft copolymer in polymer matrix has been considered to consist of thermal diffusion, segregation and surface adsorption.[2,6) It has been well established that a graft copolymer forms domain structure in the solid state. Small amount of a graft copolymer mixed in homopolymer is assumed to form a spherical domain dispersed in homopolymer matrix. In previous section, micelle formation of a graft copolymer in solution was discussed. In casting solution, the graft copolymer forms a micro domain dispersed in PSt solution due to PSt branches. During casting process, the micro domain is accumulated to the surface by diffusion and segregation.

In previous papers we pointed out that random copolymer is not so effective for the modification of polymer surfaces.7) This might be caused by insufficient mixing of the random copolymer in polymer solution and by unfavorable structure in surface adsorption. Further merit of the graft copolymer in surface modification is its resistance to migration. We measured ATR-IR spectra of modified PSt films to know the surface concentration of functional segments. Figure 4 shown ATR-IR spectra of modified PSt films before and after immersion in MeOH. The modified PSt films contained 5 wt% of the methacrylic acid copolymer. RAM is a random copolymer of methacrylic acid-MMA, the composition is 50/50 and M_n=1.9 x 10^4. In case of the random copolymer, carbonyl adsorption disappears completely in five minutes after immersion in methanol both on air side and glass side surface. However, the graft copolymer GAS-2 was scarcely extracted by methanol after three hours, showing the effectiveness of PSt branches as an anchor segment for the permanent modification of polymer surfaces.

The concentration of the graft copolymer on the polymer surface can be measured by XPS and ATR-IR. This gives further evidence for surface accumulation of functional segments. From ATR-IR spectra in Figure 4, surface concentration of methacrylic

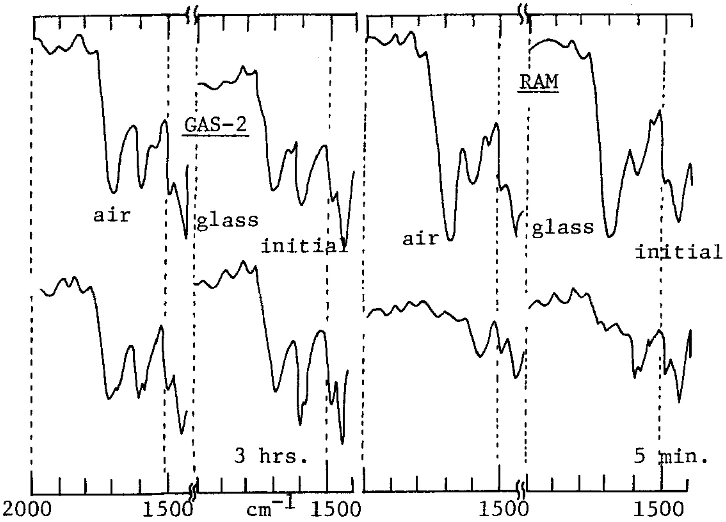


Figure 4. ATR-IR spectra of the two sides of PSt films containing 5 wt% of GAS-2 and RAM before and after MeOH immersion

acid segments can be calculated. Penetration depth of infrared light is known to depend on the wave length, but it was shown that ATR-IR spectra of this region correspond to average composition of about 2μm depth from the surface by calculation. It was apparent that the graft copolymers are concentrated on both air side and glass side of the film (40~80μm thickness). Compared to 5 wt% of the graft copolymer concentration in bulk polymer film, surface concentration was 10-15 wt% on both surface. Thus, the graft copolymers are segregated from the bulk polymer and concentrated to both side surface. This is not consistent with the contact angle measurement, where only the glass side surface is wettable. Thus wettability seems to correspond to the top surface structure of nm depth.

Spectroscopic evidence of surface accumulation of hydrophilic segments corresponding to contact angle measurement was obtained from XPS spectra. XPS spectra is known to reflect the surface composition of nm range depth. Figure 5 shows C_{1s} peak of XPS spectra of PSt film surface containing various amounts of the graft copolymer GAS-3. The air side surface and glass side surface of PSt homopolymer show similar C_{1s} peak accompanied by satelite at 292 eV. However, strong peak of C_{1s} carbonyl carbon corresponding to methacrylate group in the main chain of the graft copolymer is observed on the glass side surface of PSt film contain-

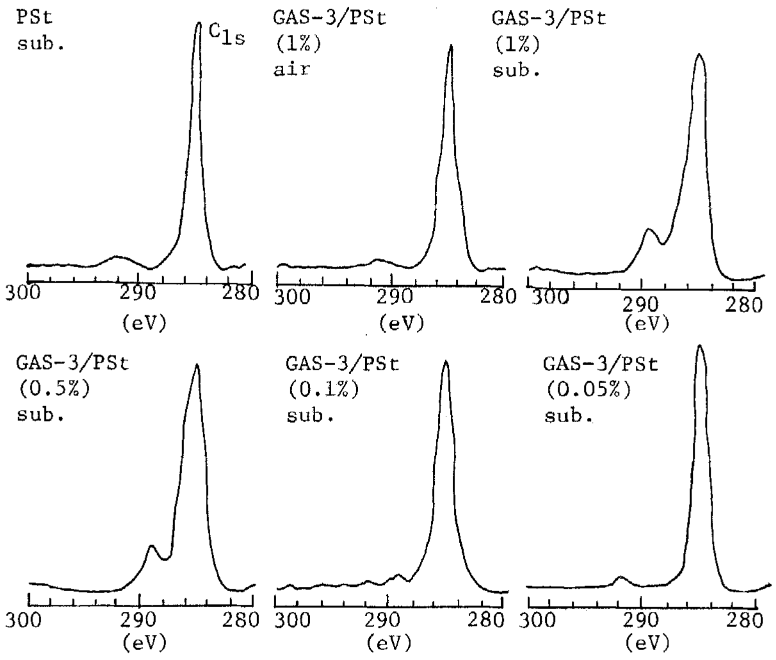


Figure 5. XPS spectra of PSt cast films containing various amounts of the graft copolymer GAS-3.
sub. means glass (substrate) side surface

ing 1 wt% of GAS-3. On the other hand, the air side surface of the same film shows si-ilar peak to PSt alone. By decreasing the concentration of added graft copolymer concentration, the change of carbonyl peak is observed. Thus the agreement of the concentration dependence of contact angle and XPS spectra is observed showing that both phenomena reflect the surface composition in nm range depth. By casting of PSt containing the graft copolymer on Teflon film, no difference were observed between air side and substrate side surface measured by contact angle and XPS. In surface accumulation of foreign substances during casting of PSt film, the participation of substrate surface is explained by the interaction of hydrophilic group of the graft copolymer and of the glass surface to change the arrangement of the hydrophilic group on the film surface. Comparison of the C_{1s} peak strength of carbonyl carbon on the glass side surface of PSt film containing 5 wt% of the graft copolymer with 100% graft copolymer film showed close similarity, and it was concluded that the surface concentration of the graft copolymer is very high and nearly equal to the backbone segment itself.

Further details of the surface structure is obtained by observing the electron micrographs. SEM shows the difference between the graft copolymer and the random copolymer. The glass side surface of PSt film containing the graft copolymer shows well dispersed small domains, but in case of random copolymer, larger domains of μm order was observed. Thus, anchor segment of the graft copolymer plays two roles in surface accumulation. One is to disperse the copolymer in small domains in polymer surface and the other is to stabilize the surface structure for migration.

Permeability of gases through surface modified membrane

The permeability of gases through polymer membrane is known to depend on the diffusion in bulk polymer and on the solubility in the polymer surface. Asymmetric membranes obtained by surface accumulation of polar graft copolymers are expected to show enhanced permeability toward polar gases by increasing the solubility coefficient in the surface.8) A graft copolymer consisting of poly MAA backbone and PSt branches (GAS-3) was blended with PSt. The membrane cast on a glass plate from the blend had a relatively non-polar air side surface and relatively polar glass side surface. The influences of this surface polarization in both sides were examined by permeation behaviors of water vapor and carbon dioxide gas and benzene vapor. The graft copolymer content in the blend was 1.0 wt% and the thickness of the cast film from THF was about 10 μm.

The permeability coefficient of water vapor through the blend membrane is plotted against relative vapor pressure p/p_0 at 25°C in Figure 6 (a). The permeability was higher when the glass side was placed toward the high pressure side in permeation cell. Permeation from air side surface was a little lower than PSt film, probably because of restricted diffusion of water vapor in PSt containing polar graft copolymers. The permeability coefficient of carbon dioxide is shown in Figure 6 (b), again showing enhanced permeation from polar side due to the increase of the solubility

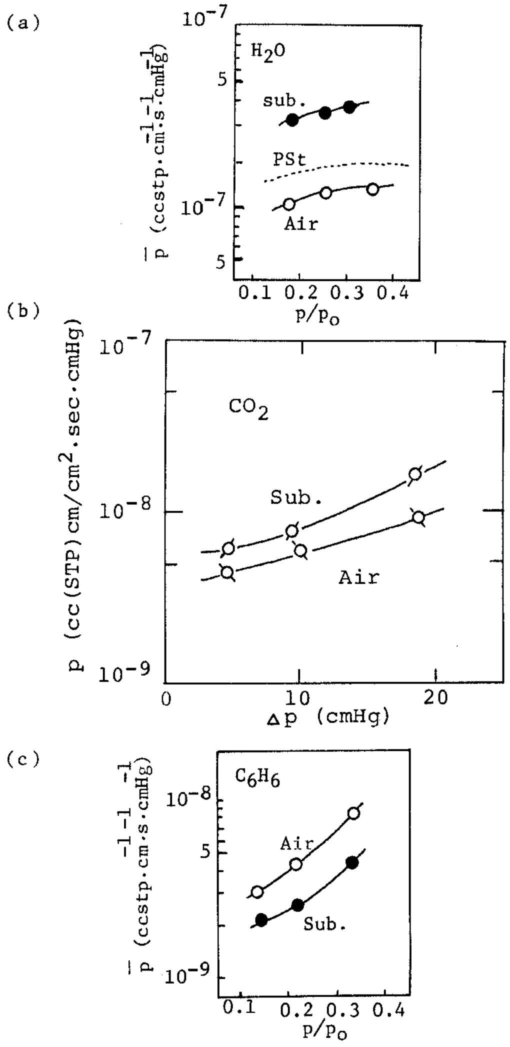


Figure 6. Permeability coefficient p of GAS-3-PSt blend (1 wt%) membrane (10 μm thickness) at 25°C. Sub denotes permeation from glass-side surface. Air from air-side surface.

coefficient. On the other hand, permeation of benzene vapor shown in Figure 6 (c) shows a different behavior. Non-polar benzene vapor is solube in PSt domain and permeation from air side is favored. These results clearly shows that the surface accumulation of polar segments on the polymer membrane by using comb graft copolymers can increase the permeability of polar gases by increasing the solubility coefficient on modified surfaces.

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