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Application of the Perturbation Molecular Orbital Method to Aromatic Oligomers and Conducting Polymers

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ABSTRACT: The perturbation molecular orbital (PMO) method has been used to calculate band gaps (E_g), ionization potentials (IP), and electron affinities (EA) of a number of electronically conducting aromatic hydrocarbon polymers. The polymers chosen were poly(*p*-phenylene) (**1**), poly(*p*-phenylenevinylene) (**2**), polyacene (**3**), poly(2,6-naphthylene) (**4**), poly(1,4-naphthylene) (**5**), and poly(perinaphthylene) (**6**). The results obtained were compared with those in the literature calculated by much more sophisticated and extensive methods and with experimental values where those were available. This method was also used to calculate E_g of a 126 carbon graphite fragment. The results show that the PMO method is quite simple, can be done rapidly, and is a very useful qualitative predictor of several electronic properties of conducting polymers. Further, it can readily distinguish those polymers predicted to have zero band gaps from those having larger ones.

Introduction

The field of conducting polymers has been the subject of major research for the past 15 years.[1,2] Organic, polymer, inorganic, and theoretical chemists have long been intrigued by the possibility of certain polymers behaving as "organic metals". It has only been recently that rational syntheses of these systems have been carried out and that theoretical chemists have attempted to calculate and predict the properties of these polymers.[3,4]

The properties of conducting polymers that one would like to accurately predict are band gaps (E_g), ionization potentials (IP), electron affinities (EA), and, less importantly, bandwidths (BW).[2] The band gap largely determines whether the polymer is intrinsically a metal, a semiconductor, or an insulator, with low band gaps required for "metal-like" behavior. For intrinsically semiconducting or insulating polymers, IP and EA are a measure of oxidizability and reducibility, respectively. Polymers that have low values of IP can be effectively doped with electron acceptors such as I_2 or AsF_5, while polymers with large values of EA can be effectively doped with electron donors such as alkali metals.[5,6] Bandwidths are a measure of electron delocalization in the polymer backbone with high values indicating high degrees of electron mobility.[7,8] However, intrachain mobility is, in general, not the limiting factor in determining the conductivity of a doped polymer but rather it is the interchain electron transfer.[9] Therefore, correlations between observed conductivities and theoretically calculated bandwidths are expected to be qualitative at best.[4]

Many techniques have been applied to the calculation of the electronic band structure of conjugated polymers. Ab initio calculations yield reliable valence band information but are not easily adapted to predict optical properties.[4,7] Also, high quality ab initio calculations require extensive computer time and are not practical for large multiatom repeat units of conjugated polymers. Semiempirical techniques such as CNDO (complete neglect of differential overlap)[10] and MNDO (modified neglect of differential overlap)[11] have been applied to conjugated polymers with some success. However, as with other semiempirical techniques, CNDO and MNDO depend heavily on parameters obtained from experimental data for small molecules and the extrapolation to polymer systems must be done with caution. A completely theoretical technique called the valence-effective Hamiltonian (VEH) technique has been successfully applied to conjugated polymers.[4,8,12,13] However, as with the above techniques, the molecular geometry must be known or readily calculated by using semiempirical techniques. Finally, a very interesting qualitative approach using perturbation theory, in which the effects of chemical substitution of atoms in conducting polymers can be estimated, has been developed by Lowe and co-workers.[14] For example, using the extended Hückel crystal orbital (EHCO) method,[15] qualitative predictions of band gaps can be performed when one C–H of poly(acetylene) is substituted by N, S, or C–F.

In this paper we discuss the use of perturbation molecular orbital (PMO) theory as a very simple alternative (paper and pencil) method to calculate E_g, IP, and EA of several conjugated hydrocarbon conducting polymers. The PMO method[16–18] is a well-established approach in dealing with chemical systems and is still used quite frequently.[19] Dewar and Dougherty (ref 16, pp. 405–7) have shown that the PMO method can successfully predict π–π^* transitions for several 1–6 ring-fused aromatic hydrocarbons, but to the best of our knowledge, the PMO method has not been applied to the study of polymeric systems.

The PMO Method

The success of the PMO method lies in the fact that it uses two odd alternant fragments A and B, each of which has a nonbonding molecular orbital (NBMO) which are, to a first approximation, degenerate. These fragments are then brought together, allowed to interact and finally to bond resulting in the formation of the new system AB (see Figure 1). There is then a first-order change in π energy

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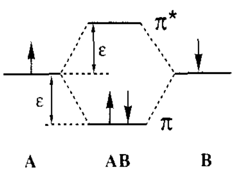

Figure 1. First-order energy of perturbation due to the union of two odd fragments A and B.

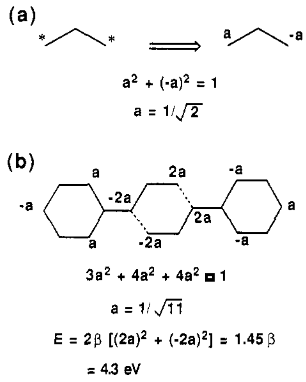

Figure 2. (a) Allyl fragment showing coefficients and normalization. (b) Combination of 1-phenylallyl fragments to give p-terphenyl.

due to the union of these odd fragments. Since first-order perturbations are much larger than second order perturbations, the union of odd fragments may be treated in terms of first-order perturbation theory alone. To this approximation, the energy of union arises entirely from interaction of the NBMO's.

The energy of perturbation (ϵ) gained through the interaction of the NBMO of odd fragments is given by eq 1, where a_{0A} and b_{0B} are the corresponding NBMO coefficients and β is the resonance integral between carbon atoms.[20] If we consider one electron from each fragment being stabilized by ϵ when forming the new molecular orbital, the π energy of the union is twice the amount in eq 1 and is given in eq 2.

$$\epsilon = \beta \sum a_{0A} b_{0B} \tag{1}$$

$$E_\pi = 2\epsilon = 2\beta \sum a_{0A} b_{0B} \tag{2}$$

An antibonding molecular orbital is also formed as a result of the perturbation, which is symmetrically destabilized by the energy amount ϵ (Figure 1). Therefore we can evaluate the electronic transition, $E_{\pi-\pi^*}$, the HOMO–LUMO energy separation, corresponding to these newly formed π orbitals as 2ϵ.

The coefficients in eq 1 can be found very simply by using Longuet-Higgins' rule for odd alternant hydrocarbons.[21] This rule states that if we star the alternate atoms, where there is one more starred than unstarred for an odd alternant hydrocarbon, and we assume that all of the resonance integrals (β) are equal for all bonds between an unstarred atom and its starred neighbors in the hydrocarbon, the sum of the NBMO coefficients vanishes. Therefore, if we arbitrarily assign the coefficient of the first carbon of an allyl fragment the value of "a", then in order for the second carbon coefficient to vanish, the third carbon coefficient should be "−a" (Figure 2a). The total energy distribution in that NBMO can be normalized and will be given by the summation of all the squared coefficients, i.e. $[a^2 + (-a)^2]$. In order to demonstrate the simplicity of the method, let us consider the oligomer p-terphenyl (1, n = 3). Partition into two symmetric fragments is shown in Figure 2b, in which the coefficients have been determined for each fragment, followed by the normalization process by which we can find the values of the NBMO coefficients and resolve eq 1. The energy found for the $E_{\pi-\pi^*}$ transition for 1 (n = 3) is 4.3 eV. Such a value depends on the value of β, which we have chosen to be 68 kcal/mol (2.95 eV), a value widely used in PMO theory for electronic transition calculations. This value of β is much higher than the 18 kcal/mol (0.77 eV) value of β used in HMO calculations. The reason for this is that PMO calculates β for the electronic transition of the HOMO–LUMO gap of benzene while HMO adopts β from the resonance stabilization energy of benzene. The interested reader may refer to ref 16 and 17 for a more detailed discussion of the value of β adopted in PMO and HMO.

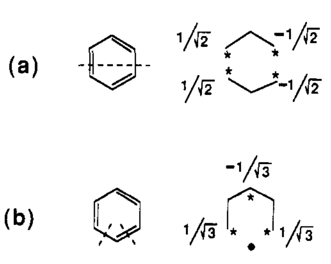

Figure 3. Formation of benzene by the union of (a) two allyl fragments and (b) a pentadienyl and a methyl fragment.

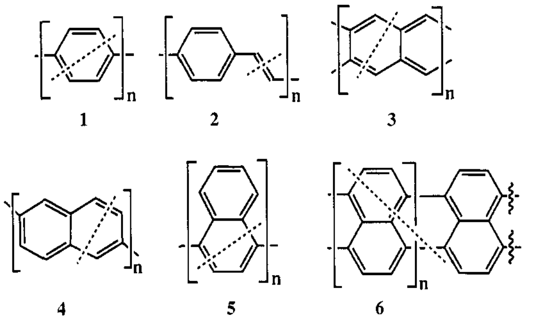

Figure 4. Conjugated aromatic conducting polymers **1**–**6**.

The principal problem with this approach is that the division of an even alternant hydrocarbon into two odd fragments can be accomplished in several ways. For example, benzene can be formed from the union of two allyl fragments (Figure 3a). By using eq 2, we obtain an $E_{\pi-\pi^*}$ of 2β (0.5 + 0.5) = 2β (HMO also predicts an $E_{\pi-\pi^*}$ of 2β). Instead, benzene could have been formed by uniting a pentadienyl radical and a methyl radical (Figure 3b) to give $E_{\pi-\pi^*} = 2\beta\ (0.58 + 0.58) = 2.3\beta$. The difference in calculating energies for the two different combinations of fragments has been attributed to second-order perturbations, which in general pushes the LUMO down in energy and the HOMO up in energy (ref 16, p 404). Therefore, the best first-order estimate of $E_{\pi-\pi^*}$ will come from the division of an even fragment into a pair of alternant fragments that minimizes the NBMO interaction. In the case of benzene, the partition Figure 3a is better since it leads to a lower value of $E_{\pi-\pi^*}$.

Results and Discussion

The polymers we have chosen to investigate are poly(p-phenylene) (**1**), poly(p-phenylenevinylene) (**2**), polyacene (**3**), poly(2,6-naphthylene) (**4**), poly(1,4-naphthylene) (**5**), and poly(perinaphthylene) (**6**). Figure 4 shows the fragments employed for **1**–**6** which best minimizes the energy of perturbation. In general, each of the monomers were extended by adding the proper fragment symmetrically such that the degree of polymerization (n) was extended from n to $n + 2$. For example, p-terphenyl (**1**, n = 3) was made by adding a benzene ring to each side of **1**, n = 1. p-Quinquephenyl (**1**, n = 5) was made by adding a benzene unit to each side of **1**, n = 3.

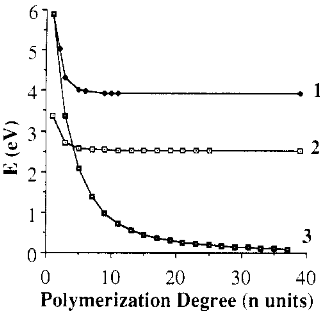

Figure 5. Plots of energy versus degree of polymerization (n) for polymers 1–3.

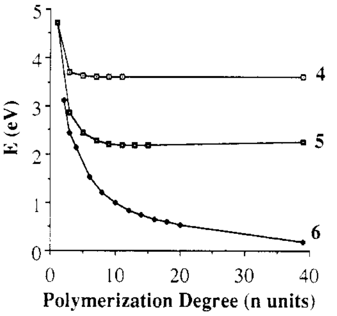

Figure 6. Plots of energy versus degree of polymerization (n) for polymers 4–6.

Table I
Band-Gap Energies (E_g) or $E_{\pi-\pi^*}$ for 1–6 (eV)

polym	DP (n)	PMO	HMO[22]	VEH[4]	PPP[23]	EHMO[24]	exptl
1	1	5.9		6.69[13]			5.90[25]
1	2	5.0		4.88[13]	4.98		4.92[25]
1	3	4.3		4.18[13]	4.52		4.43[25]
1	4	4.3					
1	5	4.0			4.05		
1	6	4.0			3.96		
1	∞	3.9	0.83	3.2[a]	3.6	1.9	3.6[26]
2	∞	2.5	0.51	2.5	3.3		3.0[4]
3	∞	0.09		0.0[b]		0.002[c]	
			0.3[c]		0.45[b]		
					0.0[d]		
4	∞	3.6	0.78				
5	∞	2.2	0.40				
6	∞	0.54		0.44[8]	0.73		

[a] Copolymer. [b] Ortho-quinoid type. [c] Para-quinoid type. [d] Delocalized.

Table II
Electronic Absorptions of Several Monomers and Oligomers

struct	DP (n)	UV λ_{max}, nm	λ_{pmo},[a] nm
1	1	204[b]	210
1	2	246[b]	250
1	3	280[c]	290
1	4	300[c]	300[d]
1	5	310[c]	310
1	6	318[c]	310[d]
1	39		320
2	(E)-stilbene	307[e]	368
3	2	286[e]	260
3	3	375[e]	370
3	4	480[f]	450
3	5	580[f]	600
4	2	253[e]	310

[a] The average error estimated from ref 16 is ±25 nm. [b] All values were obtained from ref 30. E_2 bands were mostly used, except when K bands were available. [c] From ref 28. [d] These values were obtained directly from Figure 5. [e] From ref 29. [f] From ref 31.

In Figures 5 and 6 we see plots of energy (eV) versus degree of polymerization (n) for 1–6. In each case the PMO method was used to calculate energies (eV) for degrees of polymerization up to approximately 40. Since the energies of each polymer leveled off (or very nearly so) by $n = 40$, we took these values as the band gap energy, E_g. Such a result is a consequence of the leveling off of the coefficients in the NBMO.

Table I shows the calculated PMO E_g's for polymers 1–6 along with literature Hückel molecular orbital (HMO), VEH, Pariser-Parr-Pople (PPP), extended Hückel molecular orbital (EHMO), and experimental values. Included in this table are PMO calculated E_g's for "finite chunks" of 1. When compared to the limited experimental data, it is seen that HMO and EHMO are less reliable than VEH and PPP, which predict reasonable E_g's. PMO calculated E_g's also compare quite favorably with the experimental data and with the PPP and VEH calculated data. Additionally, even though we have shown that the best value of PMO calculated E_g's are obtained from the symmetric partition of a polymer with an odd degree of polymerization, there are instances where unsymmetric partitions of a polymer with an even degree of polymerization do not deviate considerably from the energy curve. When this happens, PMO calculated E_g's also compare quite favorably with other calculated and experimental data. For example, PMO calculated E_g's of 1 (n = 2, 4, 6, and 10) deviate very little from the energy curve of 1 (n = 1, 3, 5, 7, 9, 11, and 39; Figure 5) and, therefore, accurately predicts E_g's when compared to experimental results (see Table I). This result is not general, however, and caution should be used in attempting to calculate E_g's of polymers of even polymerization degree.

One of the interesting aspects of conducting polymer research is the determination of the average length of the conjugation along the chain, which is directly related to E_g. However, the average length of conjugation in a polymer can vary considerably depending on the experimental conditions under which it is formed. Indeed, values of E_g for poly(p-phenylene) vary when it is made under different experimental conditions[27] or from different precursors,[28] and these most likely reflect different conjugation lengths. Since PMO provides the band gap for each oligomer (see Figures 5 and 6), we can compare the $E_{\pi-\pi^*}$ with available UV data of the dimers, trimers and tetramers of a specific series. Table II shows the values for the electronic transitions predicted by PMO for a series of oligomers and the values of λ_{max} observed experimentally. The average error in λ_{pmo} is generally ±25 nm (see ref 16, p 405). Although the experimental λ_{max} corresponds to the most probable transition, $E_{0,0}$ transitions are generally about 20–30 nm lower in energy at about a concentration of 0.05 g/L,[29] which puts most of the calculated absorptions closer to the experimental values. In the case of poly(p-phenylene) (1) and polyacene (3) a good correlation is observed between the experimental and calculated values. Such a close correlation further supports the E_g values obtained by our method throughout the transition from oligomers to extended linear polymers for aromatic species.

Within a conjugated polymer chain there could be defects which shorten the average conjugation length. Therefore, it is possible to have a larger average degree of polymerization, obtained from molecular weight determinations, with a much smaller effective conjugation (C_e) length of the polymer. Table III shows the reported band gap values[28] for polymers 1 and 2 made under different conditions or from different precursors. Given the energy values, we can determine the effective conjugation length of the polymer (C_e) which, if there are no experimental

Table III
Reported Band-Gap Energies for Several Polymers and PMO Predicted Average Effective Conjugation (C_e)

polym	conditions or source	E_g	C_e	ref
1	from 5,6-bis(benzoyloxy)-1,3-cyclohexadiene	3.9	6 (6)[a]	26
1	from 5,6-bis(pivaloyloxy)-1,3-cyclohexadiene	4.4	3 (3)[a]	26
1	from 5,6-bis[(methoxycarbonyl)oxy]-1,3-cyclohexadiene	3.9	6 (6)[a]	26
1	from 5,6-(diacetoxy)-1,3-cyclohexadiene	<4.1	<4 (4)[a]	24
2		3.0	3	8

[a] Numbers in parentheses are suggested values in ref 28.

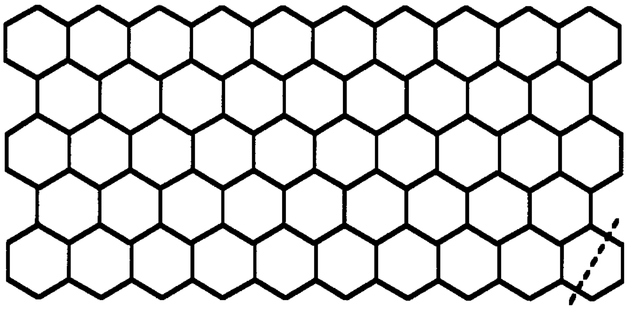

Figure 7. Graphite fragment containing 126 carbon atoms.

defects, is the same as the degree of polymerization. Notice that small effective conjugations are suggested in these cases (Table III) and PMO extrapolated C_e's compare quite favorably with reported C_e's obtained by UV spectroscopy.

Table IV shows the IP and EA calculated by PMO of 1–6 compared to VEH and PPP calculated data. Similar to the VEH treatment, PMO requires that the IP of solid-state polymers be corrected by 1.9 eV to compensate for the polarization energy of the polymer lattice. Extensive tabulations of ionization potentials of organic hydrocarbons reveal that gas phase IP's are 1.7–2.0 eV larger than the solid-state IP's.[37] When this is done, we see that PMO calculated data compares well with VEH and PPP calculated data and with the limited experimental data available for the polymeric systems. This correction is unnecessary for the simple monomers and oligomers since these measurements are not made using solids.

Finally, E_g for a 126-carbon graphite fragment was calculated by the PMO method and found to be 0.018 eV (see Figure 7). The fragments shown were used since they best minimized the energy of perturbation. The study of three-dimensional graphite has led to several different types of electronic band structures.[32–34] Although several differences appear when different interlayer packing is considered, most of the optical properties can be understood by using a single layer (two dimensional) model,[35] for which a zero band gap experimental value has been suggested (0 eV).[36] The PMO value for E_g also matches well with the calculated crystal orbital (CO) value of 0.00 eV for a two-dimensional graphite fragment.[37]

Conclusion

The PMO method has thus been shown to be a very simple and rapid, yet fairly reliable, alternative to more sophisticated techniques such as VEH and PPP in predicting electronic properties of conducting aromatic hydrocarbon polymers. Further, the PMO method does not require the use of a computer and should still prove to be a very useful tool for rapidly obtaining qualitative knowledge of the electronic properties of a large variety of polymers. It is clearly valuable, also, for distinguishing zero band gap species from others with larger band gaps.

Table IV
Ionization Potentials and Electron Affinities of Oligomers and Polymers 1–6 As Calculated by the PMO, VEH, and PPP Methods (eV)

		PMO		VEH		PPP		exptl value
polym	DP (n)	IP[a]	EA[b]	IP[13]	EA[c]	IP[23]	EA[d]	IP
1	1	8.9	3.0	9.30	2.61			9.24[33]
1	2	8.4	3.4	8.34	3.46	8.29	3.31	8.32[33]
1	3	8.0	3.7	7.97	3.79	7.91	3.39	8.20[33]
1	5	7.9	3.9			7.56	3.51	
1	6	7.9	3.9			7.49	3.53	
1	∞	5.9[e]	2.7	5.6[4,e]	2.1			5.5[4]
2	1	7.6	4.2			8.52	3.29	8.46[34]
2	2	7.4	4.4			7.79	3.59	
2	3	7.2	4.6			7.46	3.57	
2	4	7.2	4.6			7.34	3.59	
2	5	7.2	4.6			7.28	3.60	
2	6	7.2	4.6			7.25	3.63	
2	∞	5.2[e]	2.0					
3	∞	4.0[e]	3.9	3.9[4,e]	3.9			
4	∞	5.8[e]	2.2	5.3[7,e]	2.5			
5	∞	5.1[e]	2.9					
6	1	8.2	3.5					8.12[35]
6	2	7.4	4.3			7.70		6.97[36]
6	3	7.1	4.7			6.58	3.74	6.42[36]
6	4	7.0	4.9			6.04	3.81	6.11[36]
6	5	6.7	5.0			5.72	3.87	
6	6	6.7	5.2			5.52	3.91	
6	∞	4.3[e]	3.7	4.0[8,e]	3.56	5.35	3.94	

[a] $\alpha = 5.9$ eV.[32] [b] Values calculated by using PMO(IP) − PMO(E_g). [c] Values calculated by using VEH(IP) − VEH(E_g). [d] Values calculated by using PPP(IP) − PPP(E_g). [e] IP after subtracting 1.9 eV correction factor (see text).

Work is currently in progress to extend the PMO method to heteroaromatic polymer systems.

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Registry No. 1, 25190-62-9; 2, 26009-24-5; 3, 114239-77-9; 4, 28774-98-3; 5, 25322-48-9; 6, 114239-80-4; graphite, 7782-42-5.

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Permeability-Controllable Membranes. 9.[1] Electrochemical Redox-Sensitive Gate Membranes of Polypeptide Films Having Ferrocene Groups in the Side Chains[2]

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ABSTRACT: Poly(γ-methyl-L-glutamate-*co*-γ-(ferrocenylmethyl)-L-glutamate) (PMLG–Fc(x), x = 6–100%) and poly(γ-tetradecyl-L-glutamate-*co*-γ-(ferrocenylmethyl)-L-glutamate) (PC$_{14}$LG–Fc(x), x = 6–98%) were prepared from poly(γ-methyl-L-glutamate). Permeation of water-soluble fluorescent probes through PMLG–Fc(x) films cast on a platinum minigrid sheet was enhanced by a factor of 1–5 by an electrochemical oxidation of a ferrocenyl (Fc) unit in the side chains, compared with that of the reduced form. Permeability could be changed reversibly at least 20 cycles by repeated redox reactions. The extent of rate enhancements (P_{ox}/P_{red}) depended on the content of Fc side chains. Upon oxidation of Fc to Fc$^+$ side chains in the film α-helical conformations of polypeptide chains decreased and permeants could diffuse easily in the hydrophilic Fc$^+$ side-chain region or the disordered random coil polypeptide region. In the case of the PC$_{14}$LG–Fc(x) film containing both ferrocene and long alkyl chain groups in side chains, permeability was regulated by both electrochemical redox reactions and temperature changes (melting of side chains). When the anionic (NS$^-$, NS^{2-}, and NS^{3-}) and cationic (NA$^+$ and NA^{2+}) probes were employed as a permeant, storage and release phenomena of permeants were observed due to the electrostatic interaction with Fc$^+$ cations in the film by redox reactions. When the vinyl polymer having ferrocenyl groups in side chains (PFcAc) was employed as a cast film on a Pt grid, redox-sensitive permeability changes were not observed.

Biological membranes are mainly composed of lipid bilayer matrices, proteins incorporated either in the interior or on the surface, and polysaccharides adsorbed mainly on the surface. Lipid bilayers and protein molecules play important roles in the transport of specific substrates and are considered to form a "hole" or a "channel" across the membrane by molecular conformational changes responding to external stimuli.

As a model of lipid bilayer matrices, we have prepared some kinds of permeability-controllable artificial lipid membranes: a multibilayer-corked capsule membrane,[3-5] a monolayer-immobilized porous glass plate,[6,7] and a multibilayer-immobilized cast film.[1,8-10] Permeability across these artificial lipid assemblies supported by the physically strong membranes could be changed reversibly, responding to various outside effects such as temperature changes (phase transition), photoirradiation, ambient pH changes, electric field, and protein interactions.[11] These permeability controls could be explained by orientation changes of lipid matrices responding to external stimuli.

As a structural model of membrane proteins, synthetic polypeptide films have been prepared so that their permeability by the conformational change of the helical structure or the side-chain mobility could be regulated.[12-19] For example, the permeability of poly(glutamic acid)-containing polymer membranes can be affected by the conformational changes of α-helical polypeptide segments responding to ambient pH changes.[12-14] The ion permeability and membrane potential of polypeptide membranes having photoresponsive groups such as azobenzene in side

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