Anionic Conduction in Blends of Poly(Pyridinium Ethyl Methacrylate Perchloride) and Poly[Oligo(Oxyethylene) Methacrylate-*Co*-Acrylamide]

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ANIONIC CONDUCTION IN BLENDS OF POLY(PYRIDINIUM ETHYL METHACRYLATE PERCHLORIDE) AND POLY[OLIGO(OXYETHYLENE) METHACRYLATE-co-ACRYLAMIDE]

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ABSTRACT

Blends of poly(pyridinium ethyl methacrylate perchloride) and poly[oligo(oxyethylene) methacrylate-co-acrylamide] were prepared, and the ionic conductivity and mobility of the blends were investigated. Results indicate that both the transference of perchlorate anion and the dissociation of the polymeric salt in the comblike polyether obey the thermoactivation mechanism, and that the perchlorate anion in the blends is free.

INTRODUCTION

Following the report of Wright [1] on ionic conduction in complexes of poly(oxyethylene) and an alkali metal salt, the wide interest it initiated led Armand [2] to suggest that ion-conductive polymers could be used as electrolytes in all-solid batteries due to their high compliance, good adherence to the electrode, and excellent possibility of being made into thin film. The polymeric solid electrolytes investigated can be divided into two kinds: complexes of polyether and alkali metal salts called bi-ion conductors [1, 3] in which both cation and anion are mobile, and blends of polyether and polymeric alkali metal salts called single-cation conductors [4, 5], in which only the cation is mobile. Up to now, most of the reported ion-conductive polymers have been of the bi-ion type.

Although many investigations on polyether–salt complexes as electrolytes have been done in the last decade, little is known about the transference mechanism of an ion in polyether media. It was discovered that alkali metal cations can form complexes with an oxygen atom on a polyether chain, and the transference of the complexed cation was affected by the segment mobility of the polymer host [3, 6]. In a single-cation conductor in which the anion is fixed on the polymer backbone and cannot migrate, the transference of the complexed cation also depends on the mobility of the polymer segment [5]. However, the transference mechanism of an anion in polyether media has not been reported up to now. Some researchers assumed that the conduction of an anion may be compared with that of a cation, even if the anion could not form a complex with polyether [3]. In fact, some phenomena such as the temperature-dependence of the transference number [7] as well as the larger cationic transference number in plasticized polymeric electrolytes compared with unplasticized ones [8], cannot be interpreted satisfactorily by the phenomenological model described above. We reported that the temperature dependence of ionic conductivity in blends of polymeric viologen and comblike polyether obey the Arrhenius equation [9], but further work was not done because of electronic conduction in the blends.

In order to study anionic conduction in polyether media independently, blends in which only the perchlorate anion is mobile and the cation is fixed on the polymer backbone were prepared, and its anionic conductivity and mobility were investigated.

EXPERIMENTAL

Materials Preparation

Poly(Pyridinium Ethyl Methacrylate Perchloride)

2-Bromoethyl methacrylate (BrEMA) was synthesized according to the method reported by Raley [10]. BrEMA was added to a suitable amount of toluene along with azobisisobutyronitrile (1 mol% to vinyl content), and then polymerized under an N_2 atmosphere at 60°C for 24 hours. The product, P(BrEMA), was precipitated and dried at 80°C under vacuum. P(BrEMA) and pyridine in a molar ratio of 1:1 were mixed into N,N-dimethylformamide and then heated to 70°C under an N_2 atmosphere for 48 hours. Pyridine-grafted P(BrEMA), P(PyEMABr), was precipitated, dried, and then dissolved in distilled water in a flask. An aqueous solution containing 20% $NaClO_4$ was dropped slowly into the flask to precipitate P(PyEMABr) as P(PyEMAClO$_4$). The above procedure was repeated in order to obtain complete exchange. The resultant polymer, P(PyEMAClO$_4$), was washed with distilled water and dried at 80°C under vacuum for 24 hours and then stored in a desiccator for later use.

The IR spectra of P(PyEMAClO$_4$) is shown in Fig. 1. Pyridinium shows $\nu_{C=N}$ at 1640 cm^{-1} and $\nu_{C=C-H}$ at about 3050 cm^{-1}. Methacrylate shows $\nu_{C=O}$ at 1730 cm^{-1} and ν_{O-C-O} at about 1100 cm^{-1}.

The molar percentage content for each component in P(PyEMAClO$_4$) was calculated from elemental analysis (the percent contents of C, H, and N are 43.9, 5.51, and 3.52). The structure is
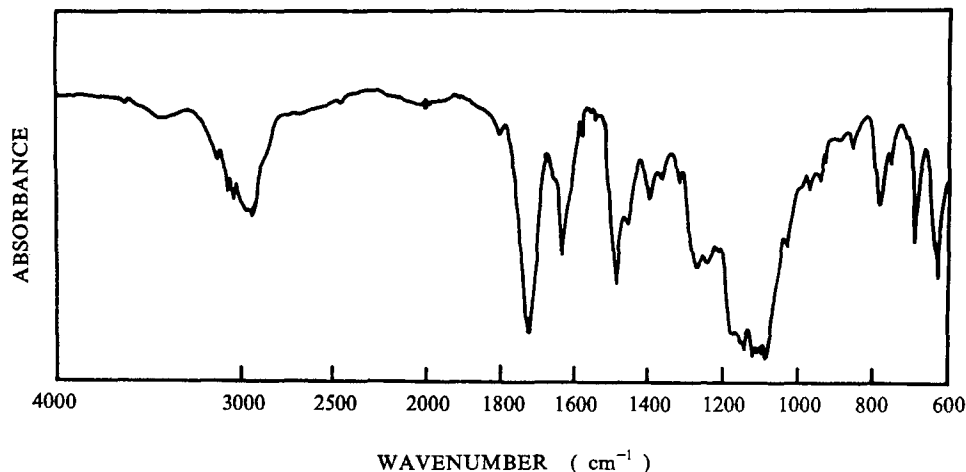
FIG. 1. IR spectra of P(PyEMAClO₄).
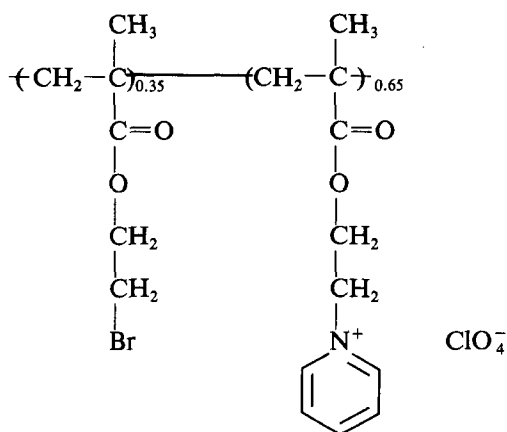
Poly[Oligo(oxyethylene) Methacrylate-co-Acrylamide]

Monomer oligo(oxyethylene) methacrylate (MEO$_{16}$, where 16 represents the number of oxyethylene units in the monomer) was synthesized in our laboratory according to a procedure described in a previous paper [11]. MEO$_{16}$ and recrystallized acrylamide (AM) were mixed at a certain proportion and then copolymerized with K$_2$S$_2$O$_8$ as initiator at 60°C in aqueous solution. The resultant comblike polyether, P(MEO$_{16}$–AM), was washed with an ethyl ether/ethanol mixture (1:1 in volume) and then dried at 80°C under vacuum. Elemental analysis yielded a copolymer composition of P(0.38MEO$_{16}$–0.62AM).

Blends of P(PyEMAClO₄) and P(MEO$_{16}$–AM)

Calculated amounts of P(PyEMAClO₄) and P(MEO$_{16}$–AM) were dissolved in methanol and stored for 24 hours. Then methanol was gradually evaporated for the formation of a homogeneous morphology. A thin film (about 100 μm) of the blends

was prepared by the hot-press method at 80 to 120°C under vacuum. All procedures dealing with the film samples as well as the subsequent measurements were handled under moisture-free conditions.

Measurements

Ionic conductivity measurements were carried out with an alternating current of 50 mV over a frequency range of 10 to 10^5 Hz. Film samples (12 mm diameter) were sandwiched between stainless steel electrodes to form a cell whose ionic conductivity was calculated from ac impedance plots. The ionic mobility was evaluated from the initial slope of the current–time curve with dc polarization for samples sandwiched between ion-blocking electrodes by the method of Kosaki [12]. Measurements of ac impedance and dc polarization at different temperatures were determined by placing the testing cells in a well-shielded, thermostated oven.

RESULTS AND DISCUSSION

Conductivity of Blends with Different P(PyEMAClO₄) Content

Since the main backbones are similar in $P(MEO_{16}-AM)$ and $P(PyEMAClO_4)$, they have good mutual solubility in a limited range. The variation of conductivity of blends with different $P(PyEMAClO_4)$ contents is shown in Fig. 2. The conductiv-
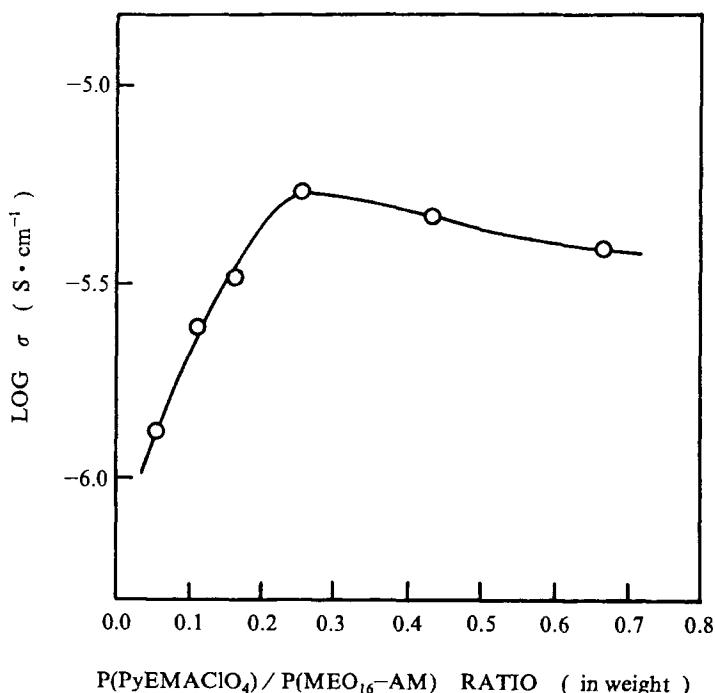

FIG. 2.   Variation of the conductivity of blends with different P(PyEMAClO₄) contents.

ity of any material can be expressed in terms of the mobility (μ) and carrier number (n) by the relationship

$$\sigma = \sum_i n_i q_i \mu_i \tag{1}$$

where q_i is the charge of carrier i. Since anions are the only carriers in this system, Eq. (1) simplifies to

$$\sigma = nq\mu$$

Pure P(MEO$_{16}$–AM) is an insulating material due to its deficiency in carriers. After P(PyEMAClO$_4$) as an ionic source was added into P(MEO$_{16}$–AM) for the formation of the blends, the solvent effect of pendant oligo(oxyethylene) in P(MEO$_{16}$–AM) promotes the partial dissociation of P(PyEMAClO$_4$) into poly-cations and perchlorate anions. Because the pyridinium fixed on the macromolecu-lar backbone as a polycation cannot migrate, only the perchlorate anion contributes to the conductivity of the blend. With increasing P(PyEMAClO$_4$) content in a blend, the carrier number (n) grows, and the conductivity rises. On the other hand, the amount of undissociated P(PyEMAClO$_4$) increases and resists the transference of the carrier with an increasing amount of P(PyEMAClO$_4$) in a blend. For this reason, both the mobility and conductivity decrease. The effects of P(PyEMAClO$_4$) content on both the carrier number and the ionic mobility lead to maximum conduc-tivity (Fig. 2).

Temperature Dependence of the Conductivity

The logarithm of the ionic conductivity of blends with different P-(PyEMAClO$_4$) contents is plotted against the reciprocal of the absolute temperature in Fig. 3. These good linear relationships infer that the ion-conductive behavior of the blends is an Arrhenius type:

$$\sigma = \sigma_0 \exp\left(-E_\sigma/RT\right) \tag{2}$$

where E_σ is the ion-conductive activation energy. The transference of perchlorate anions in the blends is similar to that of ions in aqueous solutions but different from that of a complexed cation in a single-cation conductor [4]. Since the conduc-tivity depends on the carrier number and ionic mobility, the results presented in Fig. 3 predict that both the transference of perchlorate anions and the dissociation of P(PyEMAClO$_4$) in polyether follow a thermoactivation mechanism.

The variation of the ion-conductive activation energy with the P(PyEMAClO$_4$) content in the blends, calculated from Eq. (2), was obtained from the corresponding temperature dependence of the conductivity. Figure 4 shows that the ion-conductive activation energy first rises with an increasing P(PyEMAClO$_4$) content in the blends and then stabilizes at a value of 0.52 eV. The result suggests that P(PyEMAClO$_4$) in P(MEO$_{16}$–AM) impedes the transference of the carrier. In spite of this, conductiv-ity increases with P(PyEMAClO$_4$) content in a low concentration range, as shown in Fig. 2, which means that the conductivity is mainly influenced by the carrier number rather than by the ion-conductive activation energy.
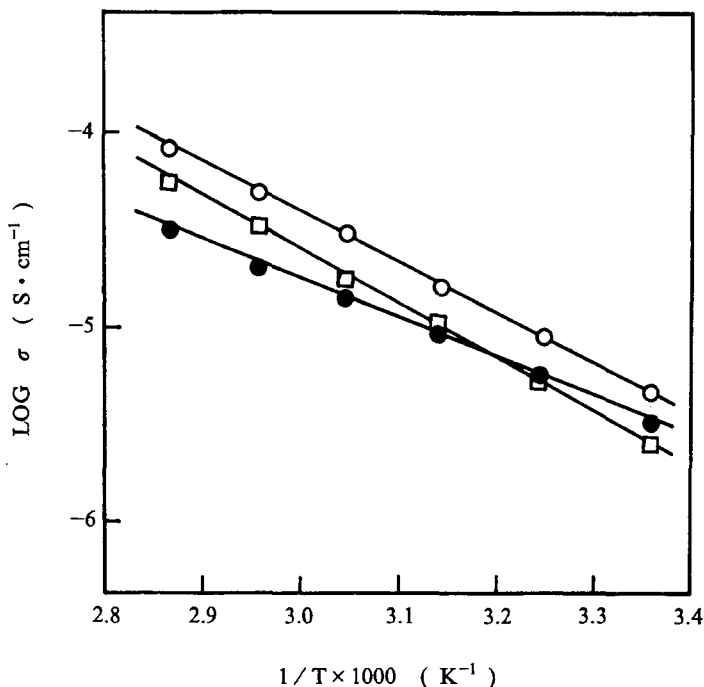
FIG. 3.   Temperature dependence of the conductivity of the blends. P(PyEMAClO₄)/
P(MEO₁₆–AM) weight ratio: (●) 10/90, (○) 20/80, (□) 30/70.

Temperature Dependence of the Mobility

In light of the study by Kosaki [12], an electrolyte in which the carrier is well
distributed was sandwiched between ion-blocking electrodes and then a dc voltage
was applied. The time dependence of the current density (i) through the electrolyte
can be expressed by

$$i = i_0 \exp\left(-\mu V^* t/d^2\right) \tag{3}$$

where V^* is the effective voltage through the electrolyte with surface area S and
thickness d, and t is the time after the application of the dc voltage. V^* is assumed
to equal the applied voltage within an initial short time. Thus, the ionic mobility (μ)
may be determined from the initial slope of the log i–t curve; it is shown in Fig. 5.
The temperature dependence of anion mobility is a straight line in an Arrhenius
diagram, which suggests that the transference of perchlorate anion obeys a thermo-
activation mechanism. The number of the activated carrier increases with an in-
crease of temperature, and thus the mobility rises. The mobility obtained is of the
same order as that of a cation in the polyether/LiClO₄ complex [3]. The transference
activation energy of the perchlorate anion (E_μ) can be calculated from the Arrhenius
equation

$$\mu = \mu_0 \exp\left(-E_\mu/RT\right) \tag{4}$$

E_μ is 0.36 eV in blends containing 25% P(PyEMAClO₄). With an increasing P-
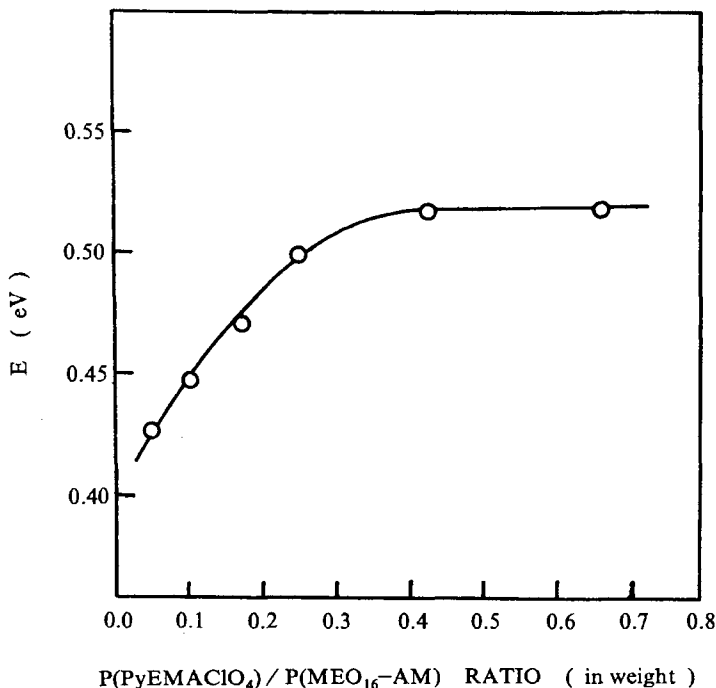(PyEMAClO₄)/P(MEO₁₆–AM) ratio, E_μ shows a gradually increasing trend.

FIG. 4. Variation of the ion-conductive activation energy with different P(PyEMAClO$_4$) content.

The diffusion coefficient (D) is related to the mobility by the Nernst–Einstein relationship

$$D = \mu RT/zF \qquad (5)$$

where z is the charge number of the carrier and F is the Faraday constant. Thus, the diffusion coefficient of the perchlorate anion in blends containing 25% P-(PyEMAClO$_4$) is estimated to be 7.2 × 10^{-9} cm$^2 \cdot$s^{-1} at 25°C. This value is larger than that of the lithium cation in a single-cation conductor [13], which could be explained by the fact that the lithium cation has been complexed while the perchlorate anion is free.

On the basis of the absolute reaction rate theory, the diffusion coefficient of the carrier is expressed as

$$D = \frac{kT}{h} \lambda^2 \exp\ (-\Delta G\ddagger/RT) \qquad (6)$$

where k, h, and R are the Boltzmann, Planck, and standard gas constants, respectively; λ is the average jump distance of the carrier. By comparing Eq. (6) with both Eqs. (4) and (5), we obtain: 1) $\Delta G\ddagger$ is the transference activation energy of perchlorate anion (E_μ), 2) $\mu_0 = zFk\lambda^2/Rh$. Therefore, λ of the perchlorate anion in blends containing 25% P(PyEMAClO$_4$) is calculated to be about 5 Å. The value is so small that the transference of an anion must be a very short distance jump process. The result demonstrates that the perchlorate anion is free in the blends.
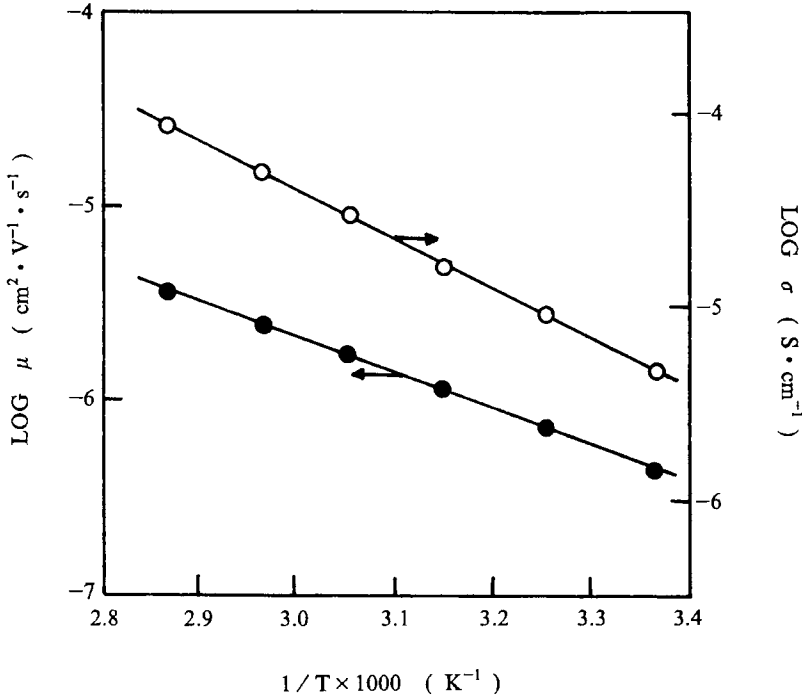
FIG. 5. Temperature dependence of the mobility (●) and conductivity (○) in blends containing 25% P(PyEMAClO$_4$).

Temperature Dependence of the Carrier Number

We can obtain the temperature dependence of the carrier number (n) from Eqs. (2) and (4):

$$n = n_0 \exp\left(-E_n/RT\right) \tag{7}$$

where n_0 is $\sigma_0/q\mu_0$ and E_n is $E_\sigma - E_\mu$. The temperature dependence of the carrier number is based on the measured conductivity and the mobility is shown in Fig. 6. The log $(n - 1)/T$ relationship exhibits a good straight line and obeys the Arrhenius equation. Since the temperature dependence of the conductivity is larger than that of the mobility (Fig. 5), i.e., E_σ is larger than E_μ, the carrier number increases with increasing temperature. The dissociation energy (E_n) calculated from Eq. (7) is 0.14 eV. The result indicates that the dissociation of P(PyEMAClO$_4$) in P(MEO$_{16}$–AM) follows a thermoactivation mechanism, which is totally different from the reported dissociation behavior of a polymeric salt in a single-cation conductor [14]. It is suggested that this phenomenon is due to the difference of complexing ability of the alkali metal cation and of pyridinium with polyether.

The total molecular number of P(PyEMAClO$_4$) in blends containing 25% P(PyEMAClO$_4$) was calculated to be 3.7 × 10^{20} cm^{-3}. According to the results shown in Fig. 6, the dissociation degree of P(PyEMAClO$_4$) in blends is about 30% at 25°C. The dissociation degree is similar to that of alkali metal salts in a polyether [15].
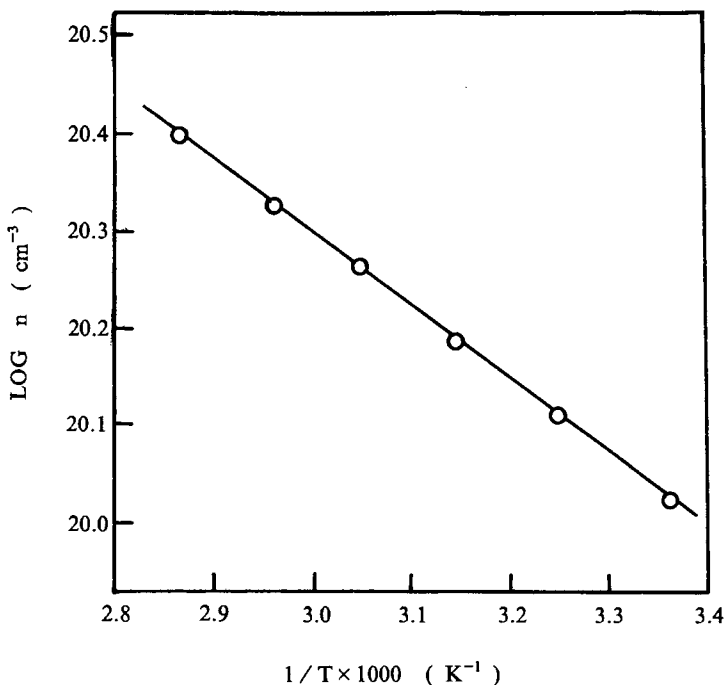
FIG. 6. Temperature dependence of the carrier number in blends containing 25% P(PyEMAClO$_4$).

CONCLUSIONS

Blends of P(PyEMAClO$_4$) and P(MEO$_{16}$-AM) exhibit high conductivity at room temperature. The temperature dependence of conductivity obeys an Arrhenius equation. Both the transference of perchlorate anion and the dissociation of P-(PyEMAClO$_4$) in the blends follow a thermoactivation mechanism. The perchlorate anion in the blends is free and it is not driven by the movement of a polymer segment.

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