Macromol. Symp. ***158,*** *125–135 (2000)*

The Influence of Elongational Flow on Hydrogen Bond Formation and Stability of the Homogeneous Phase of Binary Hydrogen-Bonded Polymer Blends

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SUMMARY: Macrophase separation tendency induced by flow in binary blends of polymers capable of single hydrogen bonding between one of the chain ends is studied analytically. To describe the conformational and orientational properties of a polymer chain a simple dumbbell model is applied. It is demonstrated that with an increase of flow rate the association rate decreases because of the extra stretching of the associated chain compared with the two initial homopolymer chains. On the other hand flow promotes association by improving the chain orientation for hydrogen bonding. As a result, at relatively weak flow the homogeneous state becomes less stable due to the decrease in the fraction of hydrogen bonded diblock copolymer-like chains. At larger flow rates the fraction of hydrogen bonded chains slightly increases enhancing to some extend the stability of the homogeneous phase.

Introduction

Mixtures of homopolymers capable of hydrogen bonding have attracted much attention recently as systems with intriguing phase behavior resulting from reversibility and strong temperature dependence of hydrogen bonding[1–11)]. Indeed, at high temperature where hydrogen bonding is hindered by considerable entropy loss, hydrogen bonded polymer blends behave as ordinary binary blends (which can be unstable with respect to macrophase separation)[1,2,5–7)]. With decreasing temperature the separation tendency increases, but at the same time hydrogen bonding becomes more favorable increasing the fraction of associated chains playing the role of compatibilisers. As a result, the homogeneous state remains (becomes) stable. At very low temperature hydrogen bonding is strongly preferable, so the fraction of associated chains becomes rather large making microphase separation possible (depending on composition)[1,2,5–7)]. The phase behavior becomes even more intriguing if the association rate can be controlled by external means. One way to accomplish this is by applying a flow field. The effect

CCC 1022-1360/00/$ 17.50+.50/0

of a uniaxial elongational flow on the association rate and the phase behavior of a mixture of homopolymers capable of single hydrogen bonding between one of the chain ends is the subject of the present analytical study.

The rheological properties of hydrogen bonded polymer systems considerably differ from that of similar systems without hydrogen bonds as is evident from experimental observations[8–11)]. One of the reasons can be the orientation dependence of hydrogen bonding: a hydrogen bond can arise only between a donor and acceptor group having the correct orientation with respect to each other[12–13)]. In the case of elongational flow polymer chains become oriented along the same direction (flow direction), which may promote hydrogen bonding between the corresponding end-groups of the polymer chains (Fig.1). This effect is of no importance for polymers capable of forming other physical bonds independent on chain orientation (such polymers we will call associated polymers below)[14–18)]. This may lead to the difference in the association rate and phase behavior between hydrogen bonded and associated polymers. But for both there is an influence of flow on the degree of association due to extra stretching of associated chains which are longer than the original non-associated chains[18)]. We will use the results obtained in the framework of a simple dumbbell model for associated polymers in the presence of elongational flow[18)] to describe the orientational properties of hydrogen bonded polymers and to define the association rate. (A more general approach involving the freely jointed model to study orientational properties and phase behaviour of associated and hydrogen bonded polymer blends will be described elsewhere[19)].) The influence of flow on the phase behaviour of hydrogen bonded polymer blends can be very complex, but in the present paper we will limit ourselves by considering only the influence of elongational flow on the association rate and through this on the phase behavior of the mixture at steady state.

Model

We will consider a binary mixture of homopolymers capable of single hydrogen bonding. Each polymer chain carries only one donor or acceptor group at the end, so that a hydrogen bonded chain resembles a diblock copolymer. Hydrogen bonding is an orientationally specific interaction, i.e. to form the bond donor and acceptor groups must have a correct orientation with respect to each other[12–13)].

Thus, if the characteristic angle φ (Fig.1) is larger than some critical value Δ ($\Delta \le 3\pi/4$)[12] no hydrogen bonds can be formed. To describe the chain conformation and orientation we will use a simple dumbbell model with a length of the dumbbell equal to the radius of gyration for a chain. Of course, for long flexible polymer chains hydrogen bonding depends mainly on the orientation of the chain segments next to the donor and acceptor groups (which will be considered elsewhere[19]) rather than on the orientation of the chains as a whole. Here we will limit ourselves by considering only relatively short chains, for which the orientation of the whole chain will be of considerable importance, taking into account that the effective rigidity ("Kuhn length") increases with an increase of flow rate.

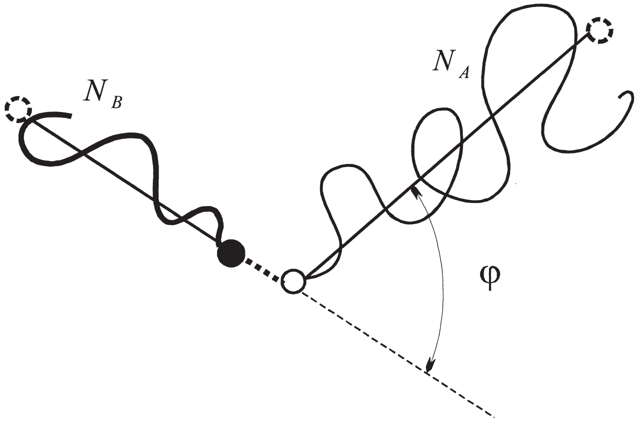

Fig.1 Schematic picture of hydrogen bonded chain

The free energy of the polymer blend in the presence of flow field can be written in the form (in units of *kT*)[18,20]

$$F = (n_A - n_{AB})[\ln(n_A - n_{AB}) + \Delta f_A] + (n_B - n_{AB})[\ln(n_B - n_{AB}) + \Delta f_B] + n_{AB}\ln n_{AB}$$

$$+ \iint n_{AB}(\theta,\theta')\left\{\ln\left(4\pi P_{AB}^{A}(\theta)\right) + U_{AB}^{A}(\theta) + \ln\left(4\pi P_{AB}^{B}(\theta')\right) + U_{AB}^{B}(\theta') - F_{AB}(\theta,\theta')\right\} d\Omega d\Omega'$$

$$+ \chi\Phi(1-\Phi) \qquad (1)$$

where n_i is the number density of homopolymers and hydrogen bonded chains, $i = A, B, AB$; respectively; $\mathrm{F}_{\mathrm{AB}}(\theta,\theta')$ is the free energy gain for hydrogen bonding and $n_{AB}(\theta,\theta')$ is the number density of hydrogen bonded chains having *A*-block oriented at the angle θ and B-block at the angle θ' to flow direction; Φ is the volume fraction of A-polymer and χ is the interaction parameter. Δf_i is the entropy loss for orientation of the homopolymer chains ($i=A,B$), $U^i_{AB}(\theta)$ is the potential acting on i-th block of the hydrogen bonded chain and $P^i_{AB}(\theta)$ is the orientation distribution function for the i-th block of a hydrogen bonded chain.

The logarithmic terms in the first line of eq. (1) describe the translational entropy of homopolymers and hydrogen bonded chains. The other terms in the first line are related to the loss of entropy due to homopolymer chains orientation. The terms in the next line characterise the entropy loss and potentials experienced by the blocks of the hydrogen-bonded chain as well as the free energy gain due to association. The last term describes the volume interactions in the polymer mixture.

The entropy loss for orientation of a polymer chain under flow

$$\Delta f_i \cong \ln\left(\frac{\alpha}{1-\exp(-\alpha)}\right) \qquad i=A,B, \qquad \alpha = 3E\overline{R}^2/R_o^2 \qquad (2)$$

has been calculated in ref.18 taking into account that the potential experienced by the chain $U(\theta)=f_{st}\overline{R}(1-\cos\theta)$ (for $0\le\theta\le\pi/2$) is defined in fact by the stretching force $f_{st}(\overline{R})=3E\overline{R}/R_o^2$ (with E being proportional to the inverse Langevin function)$^{21,22)}$. The value of the average radius of gyration of a chain under flow $\overline{R}$ $(=\overline{R^2}^{1/2})$ can be known from experimental data or theoretical analysis:$^{22)}$

$$\overline{R^2} = R_o^2\frac{(E-\beta)}{(E+\beta)(E-2\beta)} \qquad with\ \beta=\gamma R_o^2/6D \qquad (3)$$

where R_o is the average radius of gyration of a chain in the absence of flow (for Gaussian chain $R_o=N^{1/2}l$).

The potentials experienced by the blocks of the hydrogen bonded chains$^{16)}$, $U^A_{AB}(\theta)=f_{st}(\overline{R}_{AB})\overline{R}_A(1-\cos\theta)$, $U^B_{AB}(\theta)=f_{st}(\overline{R}_{AB})\overline{R}_B(1-\cos\theta)$, are somewhat larger than those for the corresponding homopolymer chains, since the hydrogen bonded chains are longer and hence more stretched by the flow. The orientation distribution functions $P^i_{AB}(\theta)$ are connected with the number density $n_{AB}(\theta,\theta')$ via

$$P_{AB}^{A}(\theta) = \iint n_{AB}(\theta,\theta')d\Omega' \big/ n_{AB} \quad ; \; P_{AB}^{B}(\theta') = \iint n_{AB}(\theta,\theta')d\Omega \big/ n_{AB}$$

$$n_{AB} = \iint n_{AB}(\theta,\theta')d\Omega d\Omega' \qquad (4)$$

where $d\Omega$ is an element of spatial angle (related to the angle θ).

The minimisation of the free energy of the polymer blend eq.(1) over n_{AB} (accounting for eq. (4)) leads to the following equation for the association rate constant K (cf.refs.2,5,18)

$$n_{AB} = K\,(n_A - n_{AB})(n_B - n_{AB}) \qquad (5)$$

where

$$K = K_{ass}K_{hb} \qquad with \quad K_{ass} = \exp\left[\Delta f_A + \Delta f_B - \Delta f_{AB}^{A} - \Delta f_{AB}^{B}\right] \qquad (6)$$

$$K_{hb} = \iint \exp\left(F_{AB}(\theta,\theta')\right)P_{AB}^{A*}(\theta)P_{AB}^{B*}(\theta')d\Omega d\Omega' \qquad (7)$$

where Δf_{AB}^{i} is the entropy loss for the blocks of the associated chain (*i=A,B*) defined by eq.(2) with $\alpha_{AB}^{i} = 3E\overline{R}_{AB}\overline{R}_{i} / R_{ABo}^{2}$ and $P_{AB}^{i*}(\theta) = \alpha_{AB}^{i}\exp(\alpha_{AB}^{i}\cos\theta)\big/4\pi\left(\exp(\alpha_{AB}^{i}) - 1\right)$ is the orientation distribution function for the blocks of an associated chain (without accounting for the orientational specificity of hydrogen bonding)$^{18)}$. K_{ass} describes the influence of flow on the association rate constant originating from the difference in the extension rates of associated and non-associated chains$^{18)}$.

In general, the free energy gain for hydrogen bonding, $\mathrm{F_{AB}}(\theta,\theta')$, is a complex function of mutual angles between donor and acceptor groups$^{12)}$. However, in order to simplify further calculations we will assume

$$\mathrm{F_{AB}}(\theta,\theta') = \begin{cases} \dfrac{H}{T} & for \quad \varphi \le \Delta \\ 0 & for \quad \varphi > \Delta \end{cases} \qquad (8)$$

Then, K_{hb} assumes the form

$$K_{hb} = \exp\left(\frac{H}{T}\right)K_{or} = K_o K_{or} \qquad (9)$$

with

$$K_{or} = \iint P_{AB}^{A*}(\theta)P_{AB}^{B*}(\theta')d\Omega d\Omega' \qquad (10)$$

In what follows we will assume that the characteristic angle Δ is relatively small, i.e. consider hydrogen bonding which is strongly orientational dependent. In this case the effect of "improved" (by flow) orientation for hydrogen bonding will be the largest. At weak flow, $\alpha^{i}_{AB} << 1$, for the mixture of polymers of similar length ($N_A \cong N_B$ and hence $\alpha^{A}_{AB} \cong \alpha^{B}_{AB} = \alpha_{AB}$) K_{or} tends to

$$K_{or} \cong \frac{\Delta \sin\Delta}{\pi}\left[\frac{\pi}{4} - \frac{\Delta}{2} + \frac{\sin 2\Delta}{4} + \frac{\alpha_{AB}}{3}(1+\cos\Delta)\right] \tag{11}$$

In the opposite limit $\alpha^{i}_{AB} >> 1$, K_{or} approaches the value

$$K_{or} \cong \frac{1}{2}\left(1-\exp\left(-\frac{\alpha_{AB}}{2}\Delta^2\right)\right)^2 + \frac{\Delta^2}{4}\sqrt{\frac{\alpha_{AB}}{\pi}}\exp\left(-\frac{\alpha_{AB}}{4}\Delta^2\right) \tag{12}$$

The dependence of $K_{or}/K_{or}(0)$ on the flow rate for different values of the critical angle Δ is presented in Fig.2. As is seen from Fig.2, K_{or} firstly slightly decreases due to the re-distribution of the polymer chains over the space angles and then steeply increases (reaching a plateau at high flow rates) as the polymer chains become more elongated and oriented. The increase is especially pronounced for smaller Δ, i.e. when hydrogen bonding is strongly orientational dependent.

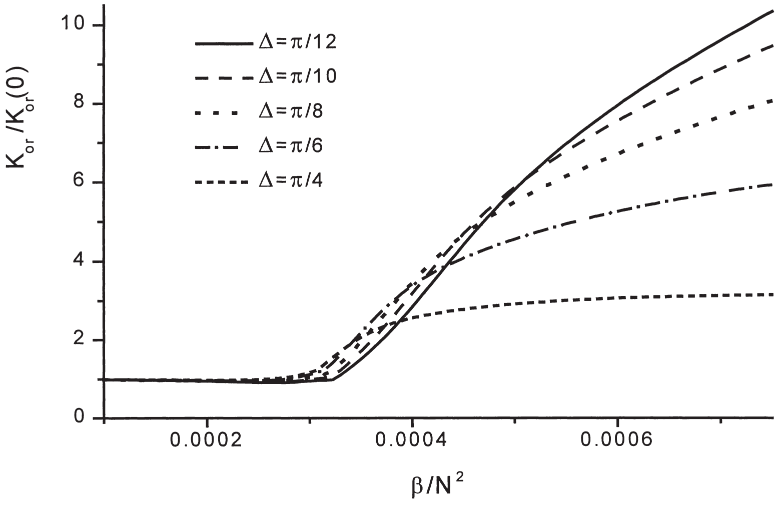

Fig.2 $K_{or}/K_{or}(\beta=0)$ vs. flow rate for hydrogen bonded polymer mixture ($N_A = 35,\ N_B = 5$) for different values of Δ.

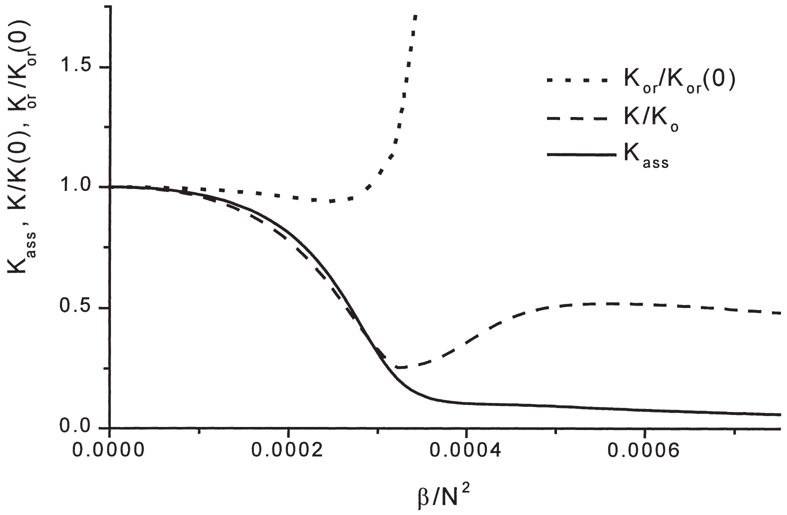

Fig.3 The association constant for hydrogen bonding $K/K(0)$, K_{ass} (the association constant due to extra-stretching of the associated chain compared to the two initial chains) and $K_{or}/K_{or}(0)$ (the association constant due to "improved orientation" of donor and acceptor groups for hydrogen bonding) for the polymer mixture ($N_A = 35$, $N_B = 5$, $\Delta = \pi/8$) vs. flow rate.

The dependence of the total association rate constant $K/K(0)$ is presented in Fig.3. At small flow rate the association constant K is close to that in the absence of flow, $K(0)$. With an increase of flow rate the blocks of the hydrogen bonded chain become more elongated and oriented than the corresponding homopolymer chains and K_{ass} decreases. K_{or} also decreases, but very slightly, so that the product, K, follows the behavior of K_{ass}. At larger flow rates the hydrogen bonded chains become considerably oriented, K_{or} increases steeply (stronger than K_{ass} decreases) and as a result the total association rate, K, also increases. At even larger flow rates, when K_{or} reaches a plateau, the association rate K smoothly decreases again because of a further decrease of K_{ass}. A comparison between associated ($K = K_o K_{ass}$) and hydrogen bonded ($K = K_o K_{ass} K_{or}$) polymer blends shows that the latter exhibits a more interesting behavior. At high flow rates the association rate may increase (due to the improvement of orientation for hydrogen bonding) while for associating polymers only a tendency to decrease for the association rate is observed.

Using eq.(5) the fraction of associated chains, $X = n_{AB} / n_A$, can be defined

$$X = \frac{1}{2}\left[A - \left(A^2 - 4\frac{n_B}{n_A}\right)^{1/2}\right] \qquad with \quad A = \frac{N_A}{K\Phi} + 1 + \frac{n_B}{n_A} \tag{13}$$

The temperature dependence of the fraction of hydrogen bonded chains in the mixture, *X*, for different flow rates is presented in Fig.4 for the same set of parameter as used in Fig.3. As it is typical for hydrogen bonding in general, the number of hydrogen bonds considerably changes with temperature. Starting from a relatively low value at high temperature (where the entropy loss is considerable) *X* increases to 1 at low temperatures, where practically all *A*-chains are associated. With an increase of flow rate the degree of association (*K*) decreases and hence *X*. This tendency is especially pronounced at high temperatures, where the energetic

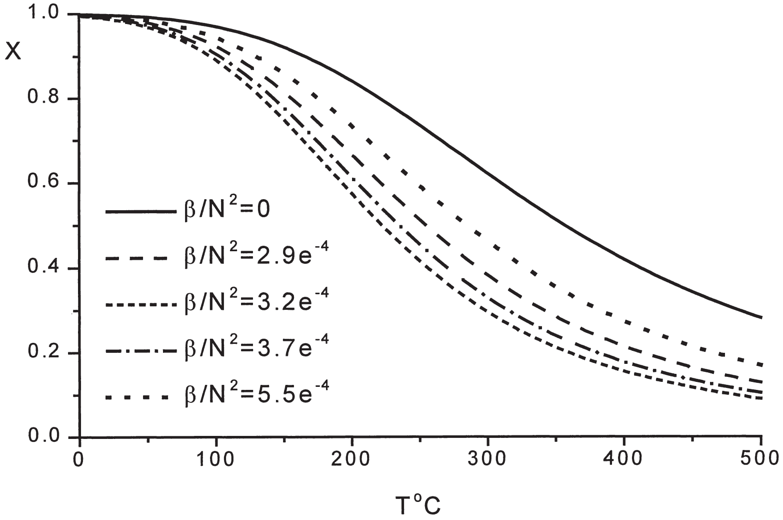

Fig.4 The temperature dependence of the fraction of hydrogen bonded chains for different flow rates ($N_{AB} = 40$, $N_A = 35$, $N_B = 5$, $H = 3200K$, $\Phi = 0.2$, $\Delta = \pi/8$)

gain for association is not so high compared with *kT*. The decrease in the fraction of associated chains *X* occurs till some critical flow rate then the increase in K_{or} (due to improved orientation for hydrogen bonding) becomes dominant over the decrease in K_{ass} (due to extra stretching of hydrogen bonded chain). At larger flow rates the fraction of hydrogen bonded chains increases till some limiting value corresponding to $K/K(0) \cong 1/2$.

As was discussed in refs.1-7 the phase behavior of hydrogen bonded polymer systems depends strongly on the association rate. If the association rate is large, i.e. the fraction of hydrogen bonded chains (playing the role of compatibilisers) is appreciable, the homogeneous state of the mixture is stable unless microphase separation is preferable for the particular mixture composition. In the presence of flow the association rate changes which influences the phase behavior as well. To characterise the stability of the homogeneous phase of the mixture of polymers with different chain length (for which microphase separation is hardly possible) the

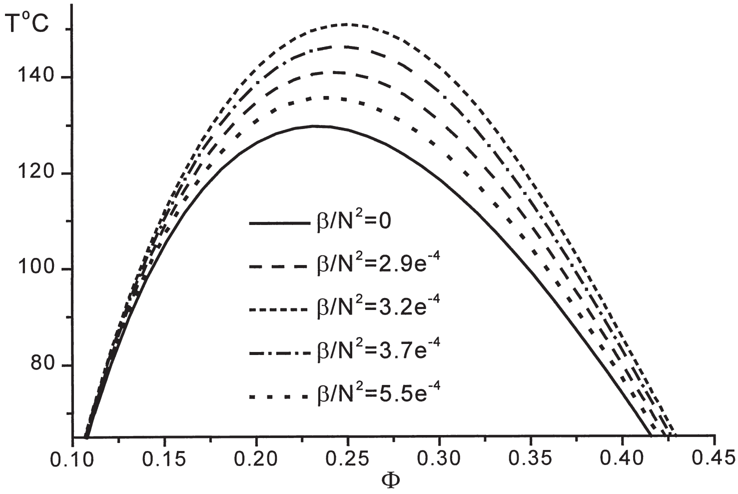

Fig.5. Spinodals for macrophase separation for the mixture of hydrogen bonded polymers ($N_{AB} = 40, N_A = 35, N_B = 5, H = 3200K,\ \Theta = 190K, \Delta = \pi/8$) under different flow rates.

spinodal of macrophase separation, i.e. the boundary of the region of absolute instability with respect to macrophase separation, can be considered

$$\left(\frac{1}{\Phi N_A}+\frac{1}{(1-\Phi)N_B}+\frac{2X}{(1-\Phi)N_A}\right)\frac{1}{1-\dfrac{\Phi N_B X^2}{(1-\Phi)N_A}}=2\chi\equiv\frac{\Theta}{T} \qquad (14)$$

Spinodals for macrophase separation for different flow rates are presented in Fig.5. In the absence of flow the homogeneous state loses stability at $130^o C$ as the highest temperature. Under increasing flow rate the degree of association and hence the fraction of hydrogen bonded chains decreases at first, so the homogeneous state becomes unstable at higher temperature; e.g. at $\beta / N^2 = 3.2e^{-4}$, the highest transition temperature is $150^o C$, which is considerably higher than in the absence of flow. With further increase of flow rate the association rate increases (due to improvement of chain orientation for hydrogen bonding) and the transition temperature decreases (till $135^o C$ as the highest temperature at $\beta / N^2 = 5.5e^{-4}$), i.e. the homogeneous state becomes more stable compared to that at $\beta / N^2 = 3.2e^{-4}$, but still less stable than in the absence of flow. Thus, the influence of flow on the phase behaviour of a mixture of hydrogen bonded polymers manifests itself in an enhancement of the segregation tendency (resulting from the decrease in the association rate), followed by a partial recovery of the stability of the homogeneous phase at larger flow rates (due to the improvement of mutual chain orientation for hydrogen bonding).

Conclusions

The influence of elongational flow on hydrogen bonding and phase behavior of polymer blends was studied analytically using a simple dumbbell model for the description of the orientational and conformational properties of a chain. It has been shown that there are two main factors contributing to the dependence of the association rate constant on the flow rate. First, since longer chains are stronger stretched (and oriented) by flow than shorter ones, association leads to a considerable additional entropy loss for associated polymer chains compared to that for non-associated chains. As a result, the association rate constant and consequently the relative fraction of associated chains decreases with an increase of flow rate. Second, strong orientation of polymer chains along the same direction at large flow rates makes it easier to form a hydrogen bond which increases the association rate. The total degree of association and hence the stability of the homogeneous phase depends on the relative contribution of both factors. Relatively weak flow enhances the instability of the homogeneous phase with respect to macrophase separation due to the decrease of association induced by extra-stretching of hydrogen bonded chains. At larger flow rates the improvement of chain orientation for hydrogen bonding leads to an increase in association rate stabilising to some extend the homogeneous state, which, however, remains less stable than in the absence of flow. Hence, applying flow it is possible to manipulate the association rate and through this the stability of the homogeneous state of hydrogen bonded polymer mixtures.

Financial support by FOM/NWO and SON/PPM is gratefully acknowledged.

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