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Polymer 40 (1999) 3585–3588

polymer

Polymer Communication

Polymer interface instability caused by a grafting reaction

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Received 16 February 1998; received in revised form 1 July 1998; accepted 1 July 1998

Abstract

We demonstrate that the interfacial tension between two molten polymers can be reduced significantly by the formation of graft copolymer at the interface by chemical reaction. If the grafting chains are short enough, the interface becomes unstable and roughens markedly, leading even to the formation of a polymer microemulsion. We investigate the onset of this roughening instability and find it that can be predicted satisfactorily by self-consistent mean field theory. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer interfaces; Graft copolymers; Interfacial tension

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1. Introduction

Phase-separated mixtures of polymers are of increasing technological interest for structural and electronic applications. Such two phase mixtures are normally prepared by mixing processes at temperatures where both phases are molten and usually consist of droplets of one phase in a matrix of the other. The interfaces between the phases are crucial in determining both the final phase size and the mechanical properties of the mixture [1]. Often graft copolymers are formed by reaction at these melt interfaces with the aim of promoting a small droplet size by inhibiting particle coalescence [2–4] and by reducing the interfacial tension [5].

The extent to which the interfacial tension γ can be reduced by copolymers formed by grafting reactions is still uncertain, however. Recently the kinetics of such reactions in the melt have been studied theoretically [6–8]. As the ratio of the interfacial excess z^* of the grafting chain to its radius of gyration R_g increases, a free energy barrier μ^*/k_BT to the grafting reaction develops due to the entropy loss involved in stretching the 'brush' of grafted chains. The build up of such a barrier as z^*/R_g increases will slow dramatically the kinetics of the grafting reaction and ultimately limit the z^*/R_g achievable in practical times. Indeed whether such a grafting reaction can lead to a z^*/R_g large enough (1.0–2.5) [9] to produce any significant decrease in interfacial tension is still in doubt; recent theoretical work [8] based on a scaling analysis valid for long grafting chains says no.

If it turns out that the interfacial tension can be strongly decreased by grafting, very interesting effects should result. A large z^*/R_g would drive the interfacial tension of the flat interface negative, leading to an instability that triggers interface corrugation and eventual formation of a polymeric microemulsion. Evidence of formation of such an interface instability caused by strong segregation of hydrogen bonding diblock copolymers to a polymer/polymer interface has been obtained previously [10, 11]; however, forming such a polymer microemulsion by a grafting reaction would be much better suited to industrial processing.

In this communication we demonstrate that it is possible to obtain large z^*/R_g by a grafting reaction using grafting chains of moderate degree of polymerization N and that once a critical z^*/R_g is reached, the interface roughens dramatically. We show that the onset of this instability can be satisfactorily predicted based on a self-consistent mean field theory estimate of the interfacial tension reduction due to grafting.

2. Experimental

Benzyl amine end-functional deuterated polystyrenes (dPS-NH_2 with $n = 55$ ($R_g = 2.0$ nm) and $n = 270$ ($R_g = 4.5$ nm) were prepared by anionic polymerization following

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PII: S0032-3861(98)00565-5

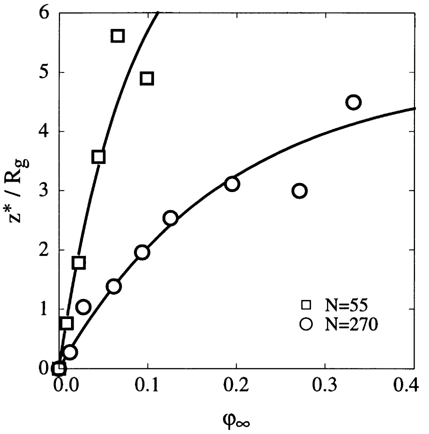

Fig. 1. Integral excess z^* of grafted chains normalized by R_g versus the volume fraction of dPS-NH$_2$ remaining in PS. Squares, $n = 55$; circles, $n = 270$. The z^* was measured after washing the PS layer off the PSMA with cyclohexane while ϕ_∞ was measured on an identical unwashed sample and was corrected for the fraction of dPS-NH$_2$ that was not amine terminated. The grafting reaction was carried out for 72 h at 190°C.

the procedure described in literature [12]. The yield of amination f was determined to be 0.6 and 0.8 for the $n = 55$ and $n = 270$ dPS-NH$_2$, respectively, by both ^{1}H n.m.r. and end-group titration. Samples for the grafting experiments were prepared as follows: films about 1 μm thick of poly(styrene-*r*-maleic anhydride) (PSMA) random copolymer with 28 wt% MA, a number average molecular weight $M_n = 52\ 000$ and a polydispersity index $M_w/M_n = 2.1$ were spun cast onto silicon wafers and dried in vacuum. Films about 0.4 μm thick of a mixture of the dPS-NH$_2$ chains and normal polystyrene (PS) of $M_n = 107\ 000$ and $M_n/M_n < 1.1$ were spun cast onto glass slides and transferred via a water surface onto the PSMA-coated wafers. The volume fraction ϕ of dPS-NH$_2$ in the PS was varied to change the initial chemical potential of the dPS-NH$_2$ in the top film. After drying, these bilayer films were annealed at temperatures above the glass transition temperature T_g of both PS (100°C) and PSMA (163°C) for various times in vacuum to allow grafting to occur. Grafting is expected to take place by reaction of the amine end of the dPS-NH$_2$ with an anhydride group on the PSMA to form first an amic acid and then ring closure occurs to form an imide [13,14].

Grafting was quantified from the deuterium depth profile measured by forward recoil spectrometry (FRES) using two methods. In the first method the interface excess z^* of dPS-NH$_2$ was determined as $\int dz(\phi(z)\text{-}\phi_\infty)$ where z is the depth from the interface and ϕ_∞ is the volume fraction of dPS-NH$_2$ in the bulk of the PS film away from the interface [15]. In the second method the bilayer film was washed in cyclohexane to remove all the PS and unreacted dPS-NH$_2$ chains. Now z^* was determined from the depth profile as the integral of dPS at the surface of the washed PSMA film [16]. The z^* values measured by both methods were in good agreement for the $n = 270$ dPS-NH$_2$ chains for all initial volume fractions and for the $n = 55$ chains for initial volume fractions less than 0.1. For $n = 55$ chains at higher volume fractions ($\phi_\infty > 0.10$) and long reaction times, z^* from method 1 was usually larger than z^* from method 2.

3. Results and discussion

The normalized grafting density z^*/R_g increases with grafting time at temperature T and then reaches an apparent saturation value at long times, increasing roughly as $z^*/R_g = A(1 - \exp(-t/\tau))$ where A and τ are constant for a given T, N and ϕ_∞. Typical values of z^*/R_g at saturation (after 72 h at 190°C) are shown in Fig. 1 for various values of the bulk volume fraction ϕ_∞ of dPS-NH$_2$ in PS. The ϕ_∞ values measured experimentally by FRES using method 1 were corrected for the fraction f of dPS chains actually terminated by amine groups. The measured z^*/R_g increases monotonically with ϕ_∞ for both the $n = 55$ and $n = 270$ grafting chains to values of approximately 6 and 4, respectively.

These values of z^*/R_g seem very large, especially considering that values of $z^*/R_g \approx 3$ for hydrogen bonding asymmetric block copolymers segregating to polymer interfaces have been associated with interface instability and microemulsion formation [10,11]. This comparison suggests that we examine the possibility that the large values of z^*/R_g observed in our grafting experiments cause a similar decrease in interfacial tension leading to interface instability as the graft copolymer at the interface builds up.

The self consistent mean field calculations of Shull [9] lead to the following result for the decrease in interfacial tension, $\Delta\gamma$:

$$\frac{-\Delta\gamma}{k_B T} = \frac{\rho_o a}{\sqrt{6N}}\,\alpha\left(\frac{z^*}{R_g}\right) \tag{1}$$

where ρ_o is the monomer number density, a is the statistical segment length of the polymer and α is a function of z^*/R_g tabulated by Shull for the limit where the unreactive matrix chains are much longer than the end-functional chains, i.e., the ‘dry brush’ regime. In what follows we use his results although we note that at large z^*/R_g, $\alpha \approx 0.5(z^*/R_g)$ [3], a result first predicted from a scaling analysis of polymer brushes by Leibler [17]. We also note that Eq. (1) is a lower limit for $-\Delta\gamma/k_B T$ because it does not consider the loss in entropy of the PSMA chains that the dPS-NH$_2$ chains are grafted to. We take the initial interfacial tension γ_o to be given by the Helfand and Tagami result [18] which is appropriate for very high molecular weight polymers:

$$\frac{\gamma_o}{k_B T} = \rho_o a \sqrt{\frac{\chi}{6}} \tag{2}$$

where χ is the Flory interaction parameter. Corrections for finite molecular weight will only decrease γ_o Dividing Eq. (1) by Eq. (2), we arrive at a very simple expression:

$$\frac{-\Delta\gamma}{\gamma_o} = \frac{1}{\sqrt{\chi N}}\,\alpha\left(\frac{z^*}{R_g}\right) \tag{3}$$

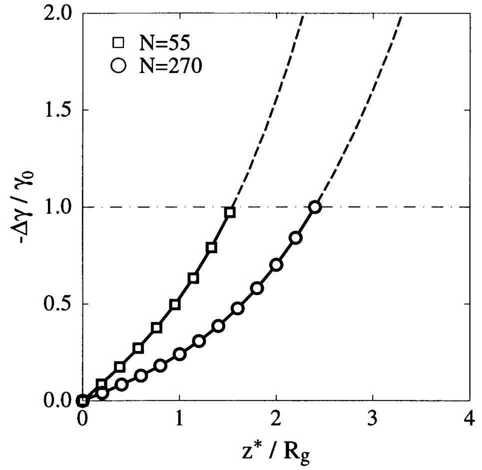

Fig. 2. Estimated ratio of the decrease in interfacial tension to the interfacial tension of the ungrafted interface from Eq. (3) as a function of z^*/R_g. Squares, $n = 55$: circles, $n = 270$.

for the ratio of the decrease in interfacial tension to the initial interfacial tension. The Flory parameter for styrene and maleic anhydride segments has been estimated to be large and positive (between 1 and 3) [19] so the effective Flory parameter between PS and PSMA is expected to be comparable to the $\chi \approx 0.1$ for the strongly immiscible polymers, PS and poly(2-vinylpyridine) [15]. As an estimate we use $\chi = 0.125$ in Eq. (3) to obtain the prediction shown in Fig. 2 for $-\Delta\gamma/\gamma_o$ vs z^*/R_g for our grafting chains. Note that $-\Delta\gamma/\gamma_o$ is predicted to exceed 1, signifying a negative interfacial tension for the flat interface above a z^*/R_g of 1.5 for the $n = 55$ chains and above a z^*/R_g of 2.5 for the $n = 270$ chains. At these critical values of z^*/R_g the grafting potential barrier μ^*/k_BT is approximately 3.4 for $n = 55$ and 5.5 for $n = 270$ [6]. At epoxy/PS interfaces that are constrained to remain flat by the crosslinking of the epoxy, $z^*/R_g \approx 3$ was observed for $n = 840$ dPS-COOH chains [16] which implies a final μ^*/k_BT barrier of about 9. Clearly at the values of N used in our present experiments, the μ^*/k_BT barrier is not so high as to prevent further reaction at the critical z^*/R_g values.

Thus we expect that the large z^*/R_g values in Fig. 1 correspond to interfaces that, if they were flat, would have negative interfacial tension. Such an interface would be unstable and low amplitude capillary waves on the interface would grow [20] until the positive curvature contributions to the interfacial tension produce a small, positive γ. The result would be a highly corrugated interface like that observed for large z^*/R_g of block copolymer segregation [10,11] Evidence that such a corrugated interface actually forms in our case is available from the scanning force microscopy of interfaces from which the PS and unreacted dPS-NH$_2$ has been selectively removed by washing with cyclohexane. As shown in Fig. 3, while the interface at low z^*/R_g is very smooth (Fig. 3a), the interface at z^*/R_g much larger than the critical value is very rough (Fig. 3b) with the scale of the lateral roughness being ~ 50 nm.

As shown in Fig. 4, a transition from a flat interface to a highly corrugated interface is found at a z^*/R_g of 2.5 for $n = 270$ chains and at a z^*/R_g of 1.8 for the $n = 55$ ones. While the values of z^*/R_g measured at the transition may not be exactly those at which $\gamma = 0$ due to the viscous nature of PSMA and the influence of large amplitude capillary waves that should be observed as $\gamma \rightarrow 0$, these results are in satisfactory agreement with the theoretical predictions shown in Fig. 2.

Thus, we conclude that significant decreases in polymer/polymer interfacial tension are possible by reaction of end-functional chains leading to graft copolymer formation at the interface. This decrease can be large enough to drive the tension of the flat interface negative, leading to formation of a deeply corrugated interface and eventually graft copolymer coated droplets. (In fact we have evidence from transmission electron microscopy of these interfaces that such

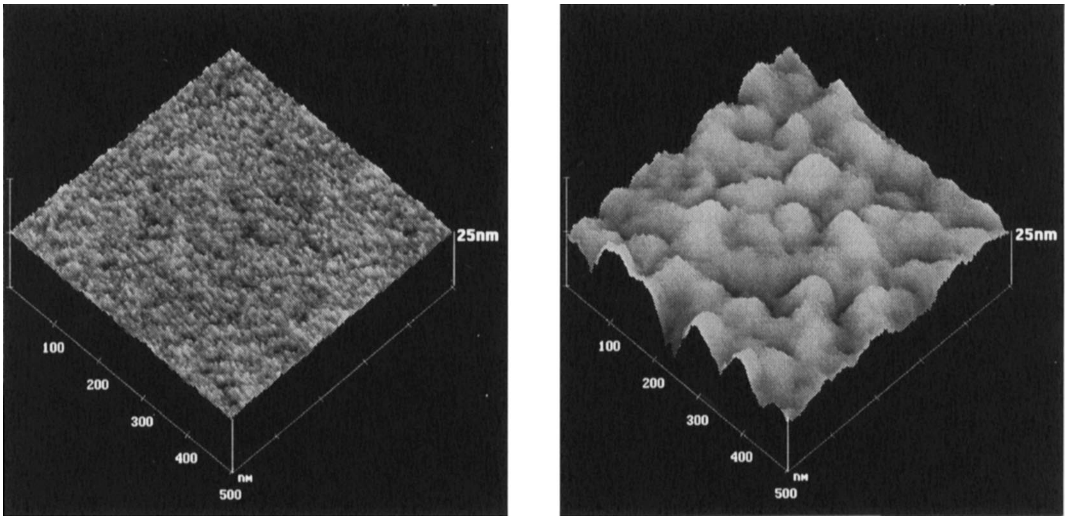

Fig. 3. Scanning force micrograph of the PS/PSMA interface grafted with $n = 55$ dPS-NH$_2$ after washing with cyclohexane. (a) z^*/R_g 0.5; (b) $z^*/R_g = 4$. The grafting reaction was carried out for 72 h at 190°C.

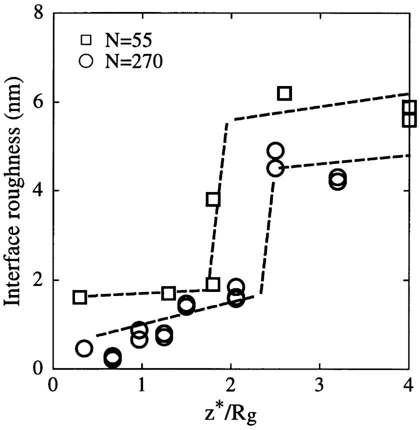

Fig. 4. The rms roughness of the PS/PSMA interface after washing with cyclohexane as measured by SFM versus z^*/R_g. Squares, $n = 55$; circles, $n = 270$. The grafting reaction was carried out for 72 h at 190°C.

droplets form. These droplets are washed away by the cyclohexane and are the reason why the z^*/R_g before washing is larger than that after washing for the $n = 55$ chains at the larger dPS-NH_2 volume fractions.) The critical z^*/R_g for vanishing interfacial tension decreases with decreasing N and for chains of moderate length, this critical z^*/R_g is attained before brush stretching decreases the reaction rate at the interface to near zero.

Acknowledgements

We acknowledge the support of the Cornell Materials Science Center (NSF-MRSEC) and its Polymer Outreach Program through fellowship support from Xerox and Universal Instruments. The work of S. de Vos was supported by Senter IOP-MT Recycling, The Netherlands. We are grateful to P. Revesz and N. Szabo of the Ion Beam Central Facility of the Materials Science Center for their help and to G. Fredrickson and B. O'Shaughnessy for helpful discussions.

References

[1] Majumdar B, Keskkula H, Paul DR, Harvey NG. Polymer 1994;35:4263.
[2] Sundararaj U, Macosko CW. Macromolecules 1995;28:2647.
[3] Beck Tan NC, Tai SK, Briber RM. Polymer 1996;37:3509.
[4] Milner ST, Xi HJ. Rheology 1996;40:663.
[5] Taylor GI. Proc Roy Soc. London A 1934;146:501.
[6] Kramer EJ. Israel J Chem 1995;35:49.
[7] Fredrickson GH. Phys Rev Lett 1996;76:3440.
[8] O'Shaughnessy B, Sawhney U. Phys Rev Lett 1996;76:3444; Macromolecules 1996;29:7230.
[9] Shull KR. J Chem Phys 1991;94:5723.
[10] Shull KR, Kellock AJ, Deline VR, MacDonald SA. J Chem Phys 1992;97:2095.
[11] Xu Z, Jandt K, Kramer EJ, Edgecombe BD, Fréchet JMJ. J Polym Sci-Polym Phys 1995;33:2351.
[12] Hirao A, Hattori I, Sasagawa T, Yamaguchi K, Nakahama S. Makromol Chem, Rapid Commun 1982;3:59.
[13] Scott C, Macosko CW. J Polym Sci-Polym Phys 1994;32:205.
[14] Jiao J. PhD Thesis, ch. 2. Cornell University (1997). Because of the high T_g of our PSMA and the relatively low grafting temperature, however, we believe that the grafting reaction in our case stops at the formation of the amic acid. At low $dPSNH_2$ volume fractions, we observe that the grafting reaction is completely reversible.
[15] Shull KR, Kramer EJ, Hadziioannou G, Tang W. Macromolecules 1990;23:4780.
[16] Norton LJ, Smigolova V, Pralle MU, Hubenko A, Dai KH, Kramer EJ, Hahn S, Berglund C, DeKoven B. Macromolecules 1999;1995:28.
[17] Leibler L. Makromol Chem-Macromol Symp 1988;16:1.
[18] Helfand E, Tagami Y. Polym Lett 1971;9:741.
[19] Aoki Y. Macromolecules 1988;21:1277.
[20] Granek R, Ball RC, Cates ME. J Phys II (France) 1993;3:829.