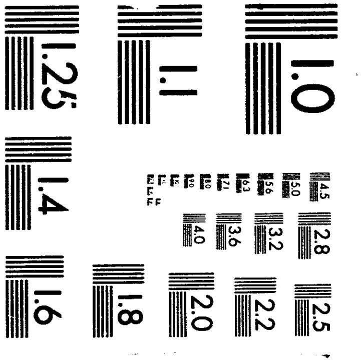
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TITLE: **STABILIZATION OF POLYANILINE SOLUTIONS**

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STABILIZATION OF POLYANILINE SOLUTIONS

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INTRODUCTION

The development of polyaniline and its derivatives in the field of conducting polymers has recently produced materials that can be formed into fibers and coatings through solution processing in organic solvents.[1] Films of polyaniline can be used for electrical devices or as corrosion resistant under coatings. One of the major difficulties in processing polyaniline solutions is that these solutions tend to gel over periods from several minutes to several hours. Many workers have observed this behavior for solutions of the emeraldine base of polyaniline (PAn-EB) in N-methyl-pyrrolidinone (NMP) and have proposed that this gelling process is due to crosslinking of the polymer chains. Such crosslinking has been attributed to formation of physical crystalline regions[2] or to the formation of chemically bonded regions through oxidative processes.[3]

With these proposed gelling mechanisms in mind we have examined the effects of including commercially available polymer stabilization additives to PAn-EB/NMP solutions. In this paper we report the effect of adding antioxidants[4] or UV absorbers[5] to PAn-EB/NMP solutions through monitoring the Brookfield viscosity over time.

EXPERIMENTAL

The emeraldine base of polyaniline (PAn-EB) was prepared by ammonium persulfate oxidation of aniline in hydrochloric acid solution using standard methods, followed by treatment with 3% NH_4OH for 2 hours[2].

The relative polymer molecular weights were determined by inherent viscosity measurements at 30.0°C in 0.1 % w/v solutions in concentrated sulfuric acid using an Ubbelohde viscometer.

The Brookfield viscosities were measured for 5 wt% PAn-EB solutions in NMP, which were prepared by stirring a mixture of PAn-EB powder and NMP for 35 minutes followed by filtration through a 60 micron in-line filter. This stock solution was then used to prepare the final solutions by mixing in the appropriate amount of additive. The antioxidant additives evaluated include sterically hindered phenols (AO-1790), hindered amine light stabilizers (HALS) (Sanduvor 3055 & 3056, Tinuvin 770 & 622), and divalent sulfur compounds (thioesters) (AO-711). The UV absorber type additives evaluated include o-hydroxy-benzophenones (UV-531), o-hydroxytriazoles (UV-2337), and o-hydroxytriazines (UV-1164). All of the additives were obtained from American Cyanamid or its subsidiary, Cytec Industries, except for the Tinuvin products which were obtained from Ciba-Geigy. Typically, the amount of additive used was 1-2 wt% based on the PAn-EB solids in solution. These final solutions were placed in a Brookfield viscometer equipped with a Brookfield UL adapter with a water jacket at 25°C. The viscosities of these solutions were monitored at regular intervals until gelation.

RESULTS AND DISCUSSION

Our initial experiments examined the relationship between polyaniline molecular weight and gel time. We noted that 5 wt% solutions in NMP could be prepared for PAn-EB with inherent viscosity (IV) of less than 0.65 dL/g which would remain fluid for several hours. However, solutions prepared fromPAn-EB with a higher IV gelled within a few minutes. The gel time for a 5 wt% PAn-EB/NMP solution is very sensitive to molecular weight as shown in Figure 1.

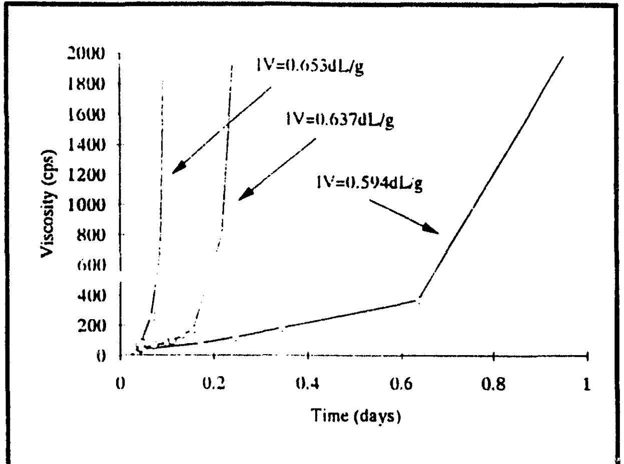


Figure 1: Effect of inherent viscosity on gelation of 5 wt% PAn-EB/NMP.

To better understand this gelation phenomenon, we studied the effect of incorporating antioxidant and UV absorbing additives on the gelation of 5 wt% PAn-EB/NMP solutions. The resultant additive solutions consisted of 2 wt% of the additive based on the polyaniline solids in a 5 wt% solution of PAn-EB in NMP. We monitored the viscosity of these solutions by Brookfield viscosity measurements until the solutions gelled. The additives that were most effective in delaying the gelation of these solutions were the hindered amine light stabilizers (HALS) as seen in Figure 2. The sterically hindered phenols and thioesters (both antioxidants), and UV absorbers have shown very little effect on the gelation of PAn-EB/NMP solutions.

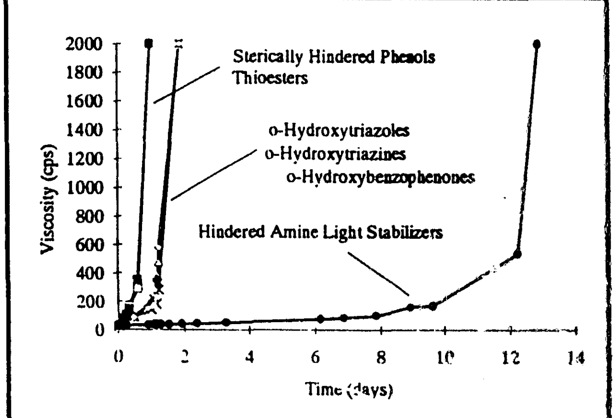
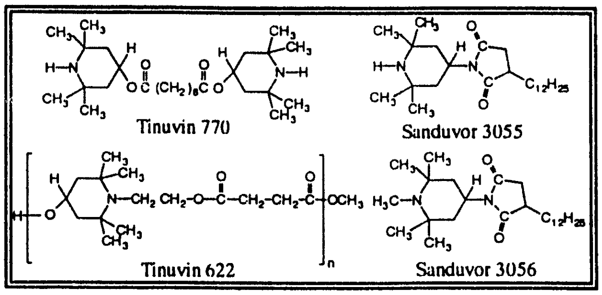


Figure 2: Effect of different additives on gelation of 5 wt% PAn-EB/NMP solutions with 2 wt% additive based on PAn-EB. Polymer IV=0.594 dL/g

Because of the increased effectiveness of the HALS additive in delaying gelation, we investigated the activity of a number of commercially available HALS additives with different chemical structures. The chemical structures, shown below, differ in substitution at the nitrogen with both Tinuvin 770 and Sanduvor 3055 containing secondary amine functional groups. The structures of both Tinuvin 622 and Sanduvor 3056 contain tertiary amine groups. We compared the activity of these HALS derivatives in delaying the gelation process in polyaniline solutions.



The solutions containing HALS additives were prepared by incorporating 2 wt% of HALS based on the polyaniline solids in a 5 wt% of PAn-EB stock solution in NMP. The viscosities of the solutions were monitored until the solutions gelled. As shown in Figure 3, HALS additives with secondary amine groups, Tinuvin 770 and Sanduvor 3055, delayed gelation, thereby, extending the useful working life of the solutions by 8-10 days. There is a direct correlation between the percentage of the hindered piperidinyl amine in the molecule and its effectiveness. This readily accounts for the difference in activity between Tinuvin 770 (5.8% N) and Sanduvor 3055 (3.4% N). The tertiary amines also follow this trend with Tinuvin 622 (5.0% N) more active in delaying gelation than Sanduvor 3056 (3.4 %N).

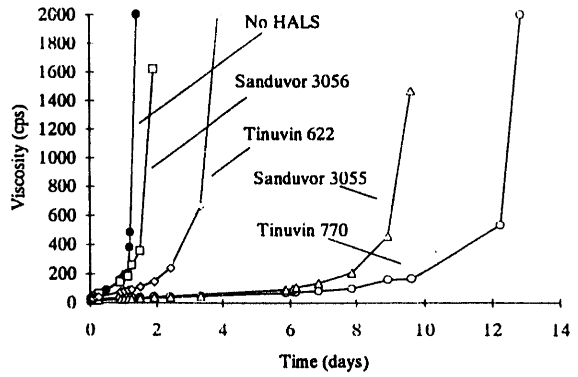


Figure 3: Comparison of hindered amine light stabilizers in delaying gelation in PAn-EB/NMP solutions with 2 wt% HALS based on PAn-EB. Polymer IV=0.594 dL/g

We further examined the effect of changing the concentration of Tinuvin 770 in the solution. Tinuvin 770 (0.5 to 10 wt% based on PAn-EB solids) was added to a 5 wt% PAn-EB/NMP stock solution. Shown in Figure 4, gelation is directly related to HALS concentration. At high concentrations of Tinuvin 770, the solution remains fluid for up to two weeks. The effect of delaying gelation is observed even at very low concentrations of additive. This is demonstrated in 0.5 wt% HALS solutions by the extenton of gelation time from several hours to greater than a day. Low additive concentrations are essential for good film properties if the solution will be used to form films or to coat substrates. In fact, thin films cast from the polyaniline solutions incorporating 2 wt% HALS additive in the solution were just as flexible as films cast from the polyaniline stock solution.

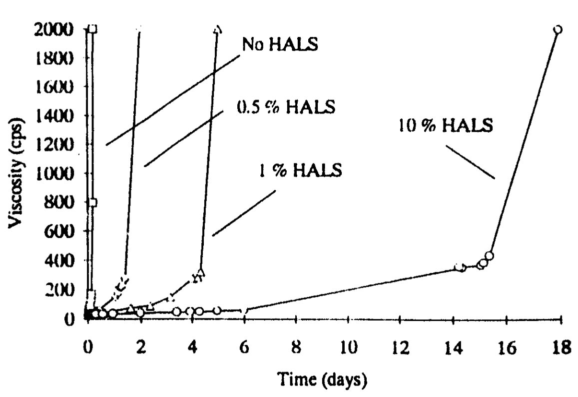


Figure 4: Effect of changing Tinuvin 770 concentration on gelation for 5 wt% PAn-EB/NMP solutions containing from 0-10 wt% HALS based on PAn-EB. Polymer IV=0.594 dL/g

Another additive commonly incorporated in polymer solutions to prevent association of polymers in solution is LiCl. If the gelling process requires polymer association prior to gelling, then this additive should be effective. We prepared a 5 wt% PAn-EB/NMP solution with 4 wt% LiCl added. This solution showed no effect in delaying the gelling of PAn-EB/NMP solutions.

CONCLUSIONS

Adding hindered amine light stabilizers to NMP solutions of polyaniline shows a dramatic effect on delaying the gelation of these solutions. However, the role of the HALS additives in delaying the gelling process of PAn-EB in NMP solutions is not well understood. We hypothesize that the hindered amine light stabilizers act in some manner other than as traditional antioxidants in preventing the gelation process. The secondary amine functional group appears to play a critical role in delaying the gelling process, perhaps, by disrupting the physical crystallization network that has been proposed to contribute to gelation. In support of this idea, a recent patent has reported the incorporation of amine or solvents to stabilize polyaniline solutions from gelation for fiber spinning applications.[6] In particular, it has been found that pyrrolidine, a secondary amine, or ammonia is an effective cosolvent with NMP in dissolving PAn-EB. We are continuing our work in stabilizing polyaniline solutions through use of additives and plan to present a comparison of the nonvolitile HALS additives with other secondary amines such as pyrrolidine.

ACKNOWLEDGMENT

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