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POLYANILINE: DEPENDENCY OF SELECTED PROPERTIES ON MOLECULAR WEIGHT

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ABSTRACT

The conductivity and tensile strength of stretch-oriented, doped, crosslinked films of polyaniline are found to be considerably greater than those prepared from non-crosslinked films of the polymer. The conductivity of the former films show little dependence on molecular weight or degree of crosslinking whereas their tensile strength shows significant dependence on these variables.

Keywords: polyaniline, molecular weight, films, gels, crosslinking, crystallinity, conductivity, tensile strength, d,l camphor sulfonic acid.

INTRODUCTION

Of fundamental importance to the whole field of conducting polymers is the relationship between molecular weight and conductivity. Very little is known about this subject although our earlier studies [1] using a preparative scale G.P.C. column to divide solutions of polyaniline (emeraldine base) in N-methyl-2-pyrrolidinone (NMP) solution into different molecular weight fractions indicated very little change in conductivity with increasing molecular weight. We have recently been developing methods [2] for controllably increasing the molecular weight of relatively large scale samples of polyaniline. The present study was directed primarily towards investigating the gelation of solutions of polyaniline under different experimental conditions and how the structural, electrical and mechanical properties of the resulting crosslinked films obtained after evaporating the solvent varied according to the nature of the film produced.

Our usual synthesis of polyaniline (emeraldine base) by the oxidative polymerization of aniline by aqueous $(NH_4)_2S_2O_8/HCl$ at ≈ 0° C results in the polymer having $\overline{M}_w \approx 64{,}000$; $\overline{M}_n \approx 25{,}000$; $\overline{M}_w/\overline{M}_n \approx 2.55$. By making the reaction solution ≈ 5 M in LiCl its freezing point can be greatly reduced and at ≈ –30° C, for example a polymer having $\overline{M}_w \approx 440{,}000$, $\overline{M}_n \approx 127{,}000$, $\overline{M}_w/\overline{M}_n \approx 3.46$ can be obtained [2]. Polymers with molecular weight intermediate between these extreme values can also be readily synthesized. The above values result from using polystyrene standards; however, light

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scattering studies show that the true $\overline{M}_w \approx 0.5$ ($\overline{M}_w$ value by G.P.C.) [3]. For convenience in the following discussions polyaniline is classified into three broad molecular weight categories — "low molecular weight," "intermediate molecular weight," and "high molecular weight" as given in Table I.

TABLE I

Molecular weight ^{a} of polyaniline (emeraldine base)

Molecular Weight	Low Mol. Wt. $\overline{M}_w < \approx 100{,}000$ $\overline{M}_n < \approx 30{,}000$		Intermediate Mol. Wt. $\overline{M}_w \approx 100{,}000 - 300{,}000$ $\overline{M}_n \approx 30{,}000 - 85{,}000$		High Mol. Wt. $\overline{M}_w > \approx 300{,}000$ $\overline{M}_n > \approx 85{,}000$	
$\overline{M}_w$	53,929	78,000	124,688	239,695	302,429	433,339
$\overline{M}_n$	21,148	26,000	34,295	81,304	92,186	126,761

(a) G.P.C. (Polystyrene standard).

POLYANILINE GELS

Gels, including polyaniline gels [4,5] are a form of matter intermediate between a fluid and a solid. We have previously described properties of polyaniline gels derived from solutions of emeraldine base in NMP by permitting the solutions to "gel" on standing at room temperature [5]. The gels are comprised of a network of polymer molecules joined in places by physical crystalline micro-domains [6]. As shown in Figures 1(a) and 1(b), the time taken for a solution of polyaniline to gel in a sealed container at room temperature decreases with (i) increasing concentration for a given molecular weight, and (ii) increasing molecular weight at a given concentration.

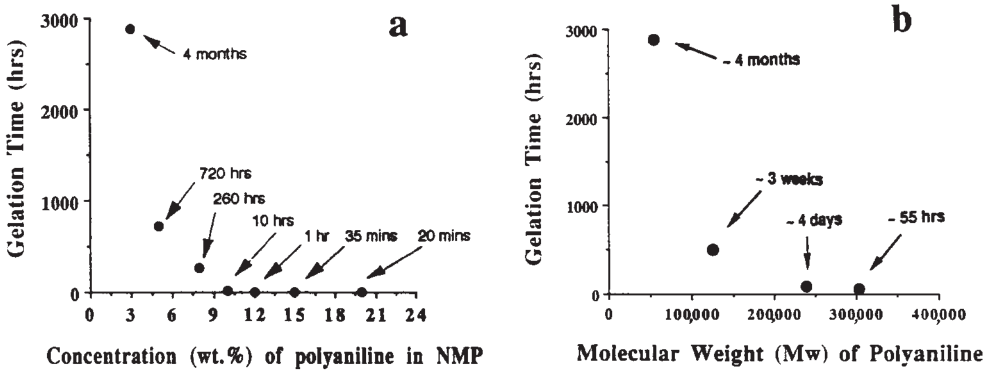

Fig. 1(a). Relationship between gelation time and wt.% concentration (in NMP) of emeraldine base ($\overline{M}_w \approx 53{,}929$).

Fig. 1(b). Relationship between gelation time and molecular weight of a ≈ 3 wt.% solution of emeraldine base in NMP.

It was also interesting to find that a 3 wt.% solution of doped polyaniline (d,l camphor sulfonic acid dopant [7]) in m-cresol also underwent gelation, exhibiting a similar gelation time/molecular weight relationship to that observed above. Thus gelation occured in ≈ 120 hrs. at room temperature using emeraldine base of $\overline{M}_w \approx 36{,}000$ but in ≈ 40 hrs. using a polymer of $\overline{M}_w \approx 144{,}000$.

CROSSLINKED AND NON-CROSSLINKED POLYANILINE FILMS

Crosslinked films can be obtained from the gels by evaporation of the NMP at ≈ 50°C. Approximately 15% NMP is permitted to remain in the film to act as plasticizer in subsequent orientation studies. Some of the polymer molecules in the films are physically crosslinked to each other by crystalline micro-domains. Those molecules involved in crosslinking are insoluble in NMP, while molecules not so involved are readily extracted by NMP from the crosslinked polymer network. As can be seen from Figure 1(a) and 1(b), the degree of crosslinking can be readily controlled by the appropriate choice of molecular weight and time. For convenience, the degree of crosslinking in films is classified by the extent of their solubility in NMP: non-crosslinked (100% soluble); slightly crosslinked (≈ 100-90% soluble); intermediate crosslinked (≈ 90-20% soluble) and highly crosslinked (< ≈ 20% soluble). That the crosslinks are physical crosslinks, not covalent bonds, is consistent with the observation that doping (with HCl) and undoping (with NH_4OH) several times breaks the physical crosslinks causing the insoluble crosslinked film to become once again completely soluble in NMP [6]. The soluble portion of the polymer was not removed from the films used in the stretch-orientation studies described below.

Non-crosslinked films are prepared by casting a film of emeraldine base on a glass substrate from an ≈ 1-3 wt.% solution of the polymer in NMP followed by removal of the solvent by a rapid stream of air at room temperature before gelation commences. They are completely soluble in NMP and are essentially amorphous. Approximately 15 wt.% of NMP is permitted to remain in the film to act as plasticizer in subsequent stretch-orientation studies.

STRETCH-ORIENTED FILMS: CRYSTALLINITY

X-ray diffraction studies were carried out using Rigaku diffractometer. It should be noted, however, that some samples which appear "amorphous" by this technique may exhibit detectable crystallinity using more sensitive x-ray techniques. All films were stretch-oriented by zone drawing at ≈ 180° C [8]. Non-crosslinked films could be stretched up to $l/l_0 \approx 12$ (l_0 = length before stretching; l = length after stretching). As can be seen from Figure 2, the films remained amorphous and were all completely soluble in NMP.

The results from stretch-orienting crosslinked films are given in Figures 3(a), 3(b), and 3(c). The solubility in NMP of all films decreased with increase of l/l_0. In all cases the most highly stretched films were completely insoluble in NMP, consistent with their significant crystallinity. Such films after doping in HCl for 48 hours followed by undoping in NH4OH for 48 hours became essentially amorphous and were almost completely soluble in NMP, indicating the destruction of the physical crystalline macro-crosslinking domains.

The crosslinked films differ remarkably from the non-crosslinked films in that a significant increase in crystallinity results during stretch-orientation. It appears that the physical crystalline micro-

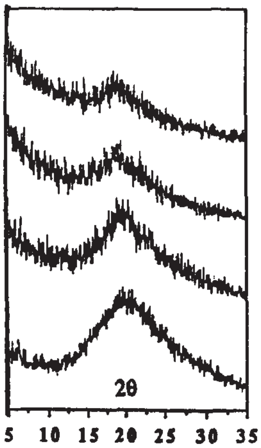

Fig. 2. X-ray diffraction spectrum of non-crosslinked film as a function of draw ratio [l/l_0 = 1.0 (bottom spectrum), 3.0, 8.0 and 12.0 (top spectrum)].

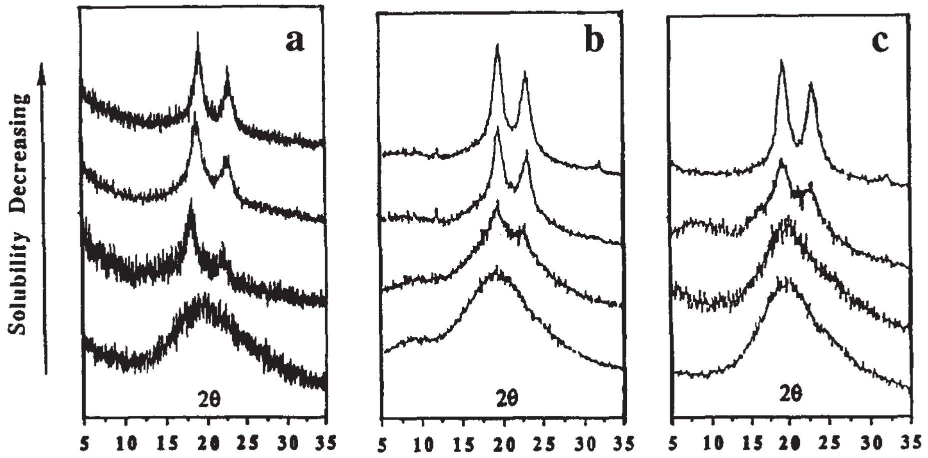

Fig. 3(a). From low mol. wt. polymer (high crosslinking) draw ratios [l/l_0 = 1.0 (bottom spectrum), 3.0, 4.5 and 5.5 (top spectrum)]. The film with l/l_0 = 1.0 was ≈ 21% soluble in NMP.
Fig. 3(b). From intermediate mol. wt. polymer (intermed. crosslinking) draw ratios [l/l_0 = 1.0 (bottom spectrum), 2.8, 3.3 and 4.0 (top spectrum)]. The film with l/l_0 = 1.0 was ≈ 26% soluble in NMP.
Fig. 3(c). From intermediate mol. wt. polymer (high crosslinking) draw ratios [l/l_0 = 1.0 (bottom spectrum), 2.0, 3.0 and 3.7 (top spectrum)]. The film with l/l_0 = 1.0 was ≈ 10% soluble in NMP.

crosslinking domains in the crosslinked films act as nucleation sites for crystallization during the stretching process.

From these as yet incomplete and on-going studies it is apparent from Figures 3(a), 3(b) and 3(c) that neither the extent of crosslinking in the films used or the molecular weight of the polyaniline employed in their preparation have any obvious major effect on their behavior on stretching. Preliminary studies, however, suggest that unstretched film derived from high molecular weight, highly crosslinked film weight might exhibit slight crystallinity.

STRETCH-ORIENTED FILMS: CONDUCTIVITY AND TENSILE STRENGTH

Major differences are observed between stretching non-crosslinked films and stretching crosslinked films. These are described in greater detail elsewhere in these proceedings [6]. It is apparent from studies performed to date as given in Figure 4(a) that the degree of crosslinking in the films used in the stretching studies and the molecular weight of the polyaniline used in their preparation have little effect on the conductivity of the doped, crosslinked stretched film. The major difference lies in whether crosslinking is or is not present in the original film used in the stretching studies. It can be seen from Figure 4(b), however, that tensile strength, not unexpectedly, is very much more dependent on the degree of crosslinking and molecular weight than is conductivity.

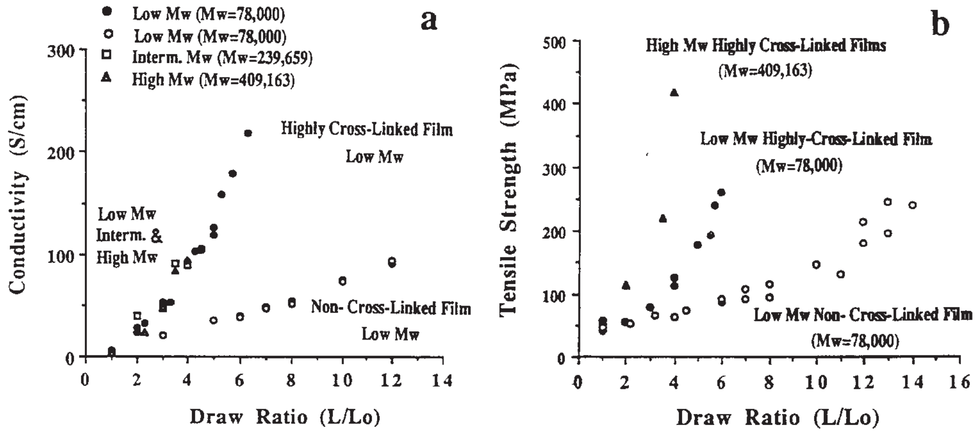

Fig. 4(a). $\sigma_{||}$ vs.l/l_0 for non-crosslinked and highly crosslinked films of polyaniline prepared from polymer with low, intermediate and high molecular weights.
Fig. 4(b). Tensile strength vs.l/l_0 for polyaniline films of different types.

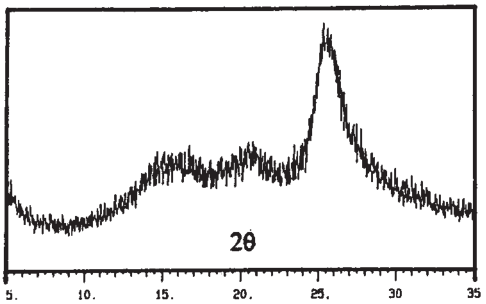

Fig. 5. X-ray diffraction spectrum of a film of doped polyaniline (d,l camphor sulfonic acid) prepared from a gel of the polymer containing m-cresol.

In summary, the importance of the present studies is that they show that the nature of the crosslinked films – their degree of crosslinking and the molecular weight of the polyaniline employed – have very little effect on the conductivity of the stretched film but have a significant effect on tensile strength.

FILMS OF POLYANILINE DOPED WITH d,l CAMPHOR SULFONIC ACID [7]

Films of the doped polyaniline prepared by evaporating m-cresol from the gel (≈ 40 hrs. gelation time) described previously were found to have significant crystallinity (Figure 5) without stretching and exhibited a conductivity of ≤ ≈ 150 S/cm. They were essentially insoluble in m-cresol. Hence, again an increase in crystallinity is paralleled by an increase in conductivity.

CONCLUSIONS

Stretch-alignment of non-crosslinked polyaniline films results in an amorphous polymer exhibiting surprisingly large conductivities and tensile strengths. Alignment of crosslinked films results in the appearance of significant crystallinity and still larger increases in both conductivity and tensile strength. The degree of crosslinking and the molecular weight of the polyaniline appear to have little direct effect on conductivity in crosslinked films but a significant effect on tensile strength. It is also possible in special cases to find significant crystallinity in non-stretched polyaniline films.

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REFERENCES

1 E.M. Scherr, A.G. MacDiarmid, S.K. Manohar, J.G. Masters, Y. Sun, X. Tang, M.A. Druy, P.J. Glatkowski, V.B. Cajipe, J.E. Fischer, K.R. Cromack, M.E. Jozéfowitz, J.M. Ginder, R.P. McCall and A.J. Epstein, Synth. Met., 41, 1991, 735.
2 S.K. Manohar, A. Fagot, A.G. MacDiarmid, R.C.-Y. King and A.J. Epstein, Bull. Am. Phys. Soc., 37, 1992, 506.
3 C.H. Hsu, S.K. Manohar, A.G. MacDiarmid and A.J. Epstein, manuscript in preparation.
4 O. Oka, S. Morita and K. Yoshino, Jap. J. of Appl. Phys., 29, 1990, 679.
5 A.G. MacDiarmid, S.K. Manohar, E.M. Scherr, X. Tang, M.A. Druy, P.J. Glatkowski and A.J. Epstein, Polym. Mat.: Sci. and Eng., 64, 1991, 254.
6 A.G. MacDiarmid, Y. Min, J.M. Wiesinger, E.J. Oh, E.M. Scherr and A.J. Epstein these Proceedings.
7 Y. Cao, G.M. Treacy, P. Smith and A.J. Heeger, Appl. Phys. Lett., 60, 1992, 2711; Y. Cao, P. Smith and A.J. Heeger, Synth. Met., 48, 1992, 91.
8 T. Kunugi, T. Kawasumi and T. Ito, J. Appl. Polym. Sci., 40, 1990, 2101.