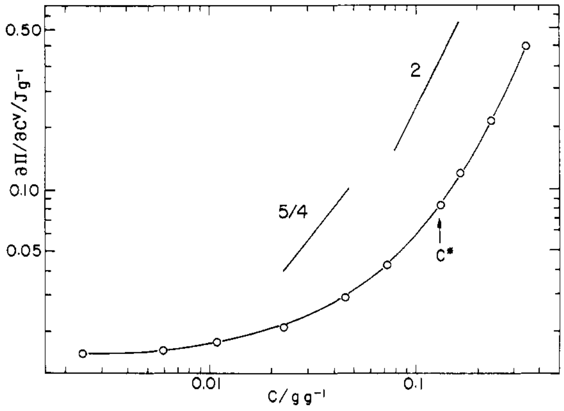

Figure 1. A plot of osmotic compressibility as a function of concentration for the polystyrene-*trans*-decalin system at 30 °C.

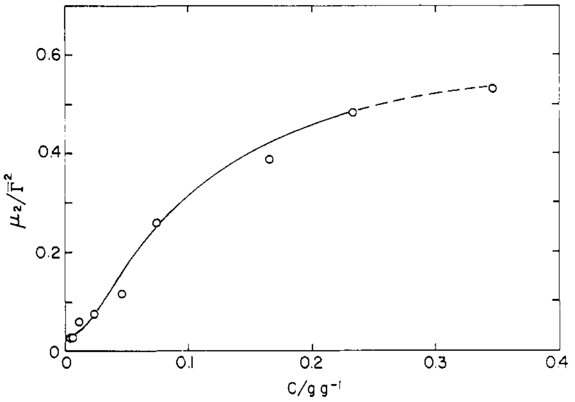

Figure 2. A plot of $\mu_2/\bar{\Gamma}^2$ vs. concentration for the polystyrene-*trans*-decalin system at 30 °C. All measurements were performed at $\theta = 90°$ except for the concentration at 34.5 wt % polystyrene where we used $\theta = 135°$. Values of $\mu_2\bar{\Gamma}^2$ at high concentrations are approximate, as the cumulants expansion does not provide a good representation of the entire correlation function profile.

In a recent study,[15] we have established that the value of the asymptotic critical exponent β of a polymer solution (polystyrene with $\bar{M}_w = 1.56 \times 10^6$ in cyclohexane) be like that calculated for the Ising model provided that we use extended scaling.[16] Thus, it would be unreasonable to expect the limiting simple scaling relations to hold over the entire temperature-concentration diagram. The deviations suggest that we need correction terms (extended scaling) to simple scaling in order to predict generalized polymer solution behavior of finite molecular weights. A more detailed study and analysis of static and dynamical properties of polystyrene in *trans*-decalin is in progress.

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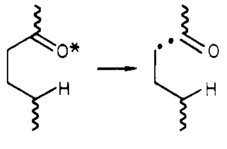
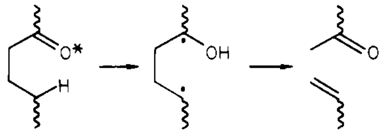
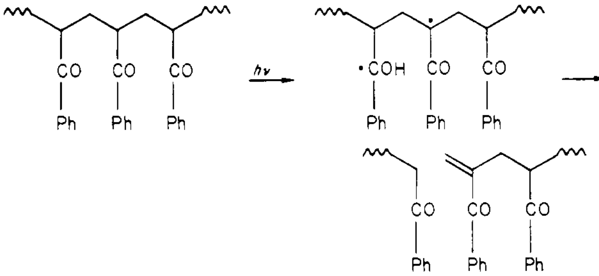
Photoenolization in Polymers. A Simple Way to Reduce Photodegradation

The elementary processes involved in polymer photodegradation frequently reflect the chemistry of excited carbonyl groups, particularly the Norrish type I and type II processes, reactions 1 and 2.[1]

type I

(1)

type II

(2)

In triplet state reactions the type II process tends to be more important whenever the C–H bond dissociation energy at the γ position is relatively low (e.g., tertiary hydrogens).[2] The photodegradation of poly(phenyl vinyl ketone), PPVK, is a typical example of this type of behavior, reaction 3.[3,4]


(3)

We have examined the possibility of using the high reactivity of carbonyl triplets in hydrogen abstraction processes in order to *prevent* the photodegradation. This can be achieved if a suitable reversible process can be found, which would effectively behave as an energy sink. The photoenolization of the *o*-methylbenzoyl group shows precisely this property,[5] and this communication reports the results of a comparative study of the photochemistry of PPVK, poly(*o*-tolyl vinyl ketone) (PTVK),[6] and a copolymer containing 11:89 tolyl vinyl ketone–phenyl vinyl ketone (Co-PT).[7]

The deaerated samples were irradiated in benzene at 30 °C with light of 366 nm using a high pressure mercury lamp and monochromator. Typical radiation dose rates were ca. 1-5 × 10^{-6} einstein L^{-1} s^{-1}.[8] Figure 1 shows a plot of the number of bonds cleaved (formally "moles" of

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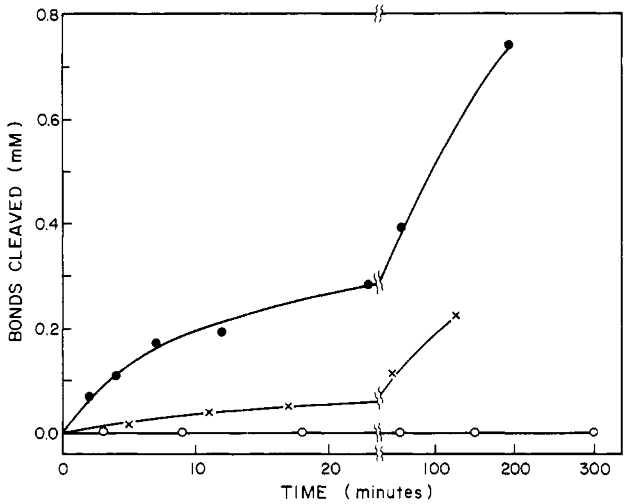
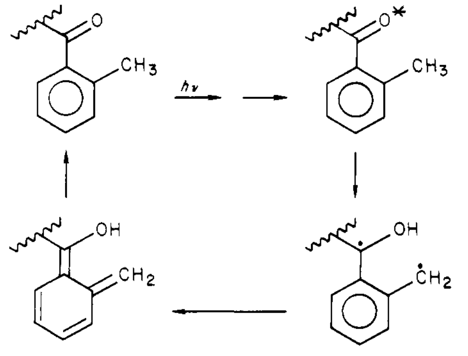


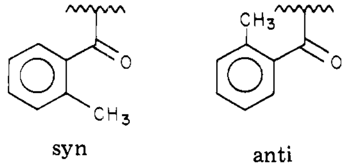
Figure 1. Rates of bond cleavage under constant experimental conditions: (●) PPVK, (X) Co-PT, (O) PTVK. The ordinate (in millimolar units) was calculated as the product of the number of bonds cleaved per initial macromolecule times the initial molar polymer concentration; it is effectively the concentration of CH_2=C(COPh) groups.

bonds) vs. time. Quite clearly PTVK undergoes no detectable photodegradation even after lengthy irradiation. We attribute the stability of PTVK to reversible photoenolization,



(4)

These processes are well known in the case of small molecules.[5] Typically, two triplet states are observed corresponding to the syn and anti conformations of the tolyl group with respect to the carbonyl chromophore.[9]



The syn conformer usually has a very short triplet lifetime (subnanosecond range) due to rapid enolization involving the abstraction of the benzilic hydrogens. On the other hand the lifetime of the triplet for the anti conformation is controlled by the rate of bond rotation to the syn conformer (typically 10–50 ns).[9a] When γ-hydrogen atoms are available, the Norrish type II process competes with the rotationally controlled decay of the anti conformation.[9a,10]

In the case of the homopolymer (PTVK) we have observed no evidence for type II fragmentation. It is conceivable that the energy is transferred along the polymer, through anti conformations of the substituents, until the energy sink, a syn conformation, is reached, from which photoenolization takes place. In other words, energy migration appears to be substantially faster than either bond rotation or the Norrish type II reaction.

In the case of Co-PT we find that when approximately 1 in 9 of the benzoyl groups is ortho substituted, nearly 90% of the initial photodegradation is prevented (see Figure 1).[11] The rate of the type II process in the homopolymer, PPVK, has been estimated as 5.9×10^7 s^{-1}[4a] and should be similar in the copolymer. Our evidence indicates that incorporation of a small number of *o*-methyl substituents substantially decreases photodegradation. This must reflect a very rapid migration of the triplet energy along the polymer, which in order to compete favorably with the type II process must have a "residence time" of less than 1 ns in any given chromophore.

In general we would expect four parameters to play important roles in controlling the efficiency of *o*-methylbenzoyl groups as photostabilizers: (i) absorption characteristics of the *o*-methylbenzoyl group in comparison with other chromophores present in the polymer; (ii) rate of energy migration, a process that could be expected to be slower in systems with nonsequential carbonyl chromophores; (iii) rates of competitive processes when they lead to degradation rather than energy wasting; and (iv) distribution of photoenolizable groups, higher efficiency being expected for statistically distributed groups. Experiments are presently underway to test the magnitude of these effects.

In conclusion, we note that the *o*-benzoyl group leads to polymer photostabilization when excited directly or as a result of energy migration within the polymer. The stabilization results from the reversibility of photoenolization and is effective even when in competition with rather fast photodegradative processes.

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(12) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-1932 from the Notre Dame Radiation Laboratory.

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Colloid Titration Behavior of Poly(ethyleneimine)

Poly(ethyleneimine) (PEI) is a branched polymer and thus contains primary, secondary, and tertiary amino groups. From the study on the polymerization mechanism, Dick and Ham[1] showed that the ratio of primary, secondary, and tertiary amino groups was 1:2:1. This was confirmed by Lukovkin et al.[2] from the result of NMR study. The dissociation behavior[3-5] of the amino groups in PEI was evaluated by potentiometric titration and was known to be different from other polyacids and polybases.

In the present study, the mechanism of the formation of polyion complex between PEI and a linear polyanion was investigated by means of the colloid titration which was originated by Terayama.[6] Potassium poly(vinyl alcohol) sulfate (KPVS) was used as the linear polyanion. The result of the colloid titration was compared with that of the potentiometric titration, and the stoichiometry of the salt-linkage formation between three amino groups in PEI and $-OSO_2O^-$ groups in KPVS was discussed.

Experimental. PEI was obtained from Tokyo Kasei Kogyo Co., Ltd. The polymer was fractionated and purified in the same manner as described in the literature.[7] The weight-average molecular weight of the fraction used here was 1.1×10^5, as estimated by the viscometric measurement.[5] The result of elemental analysis was: H, 11.9; C, 55.7, N, 32.4. These values agree with those (H, 11.6; C, 55.8; N, 32.6) calculated by the assumption that the PEI contains 25% of primary and tertiary amino groups and 50% of the secondary amino group. The physical properties of KPVS were already characterized in the previous study.[8] The degree of esterification for KPVS was 0.924, as estimated from the sulfur content (19.3%).

The colloid titration was carried out at 25 ± 0.1 °C in a nitrogen atmosphere using a Hirama Automatic Recording Titrator. The PEI (0.211 mg) was dissolved in 50 mL of distilled water, and then the pH of the solution was adjusted with 0.1–1 M HCl and NaOH. The sample was titrated with 0.00252 N KPVS solution adjusted to the pH of the sample. The end point of the titration was indicated by the turbidimetric and conductometric measurements.

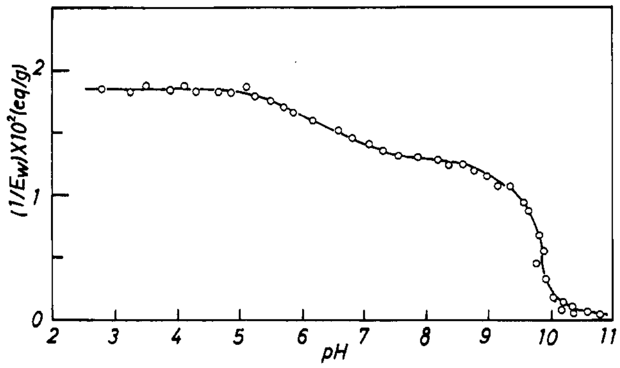

Figure 1. Colloid titration curve of PEI with KPVS at ionic strength of 0.

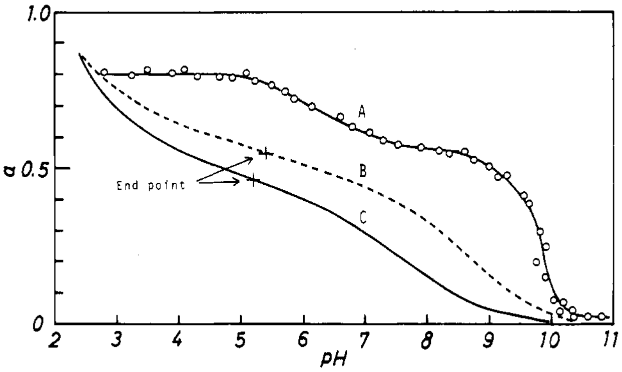

Figure 2. The curves of α vs. pH. Curve A (ionic strength 0) was obtained from Figure 1. Curve B (ionic strength 0.1) and curve C (ionic strength 0) were calculated from the results of potentiometric titrations by the following equation: $\alpha = \alpha_n + (C_{OH^-} - C_{H^+})/C_P$, where α_n represents the degree of neutralization, C_{H^+} and C_{OH^-} are the molarity of protons and hydroxyl ions, and C_P is the molar concentration of the total amino groups in PEI.

The potentiometric titration was also carried out to investigate the dissociation behavior of the amino groups in PEI. The sample solution (containing 8.98 mg of PEI in 50 mL of solvent) was titrated at 25 ± 0.1 °C in an atmosphere of nitrogen with 0.107 N HCl using a Toa-denpa Automatic Titration Apparatus (Model HMS-10A pH stat equipped with Model XYR-2A recorder). The ionic strength of the titration system was adjusted with NaCl.

Results and Discussion. The colloid titration curve was obtained by plotting the reciprocal of equivalent weight (E_w) of PEI against pH. The result is shown in Figure 1. The curve has three plateaus at the regions of pH <5, 7.5–8.5, and >10.5. The electrophoretic study of KPVS in the previous paper[8] showed that the dissociation of $-OSO_2O^-$ groups in KPVS is independent of pH in the region of 3–11. Therefore, it is considered that the change of $1/E_w$ on pH can be related to the dissociational change of three amino groups in PEI.

In order to investigate the mechanism of complex formation between PEI and KPVS, the relation between pH and the degree of dissociation (α), which was calculated by $\alpha = (1/E_w)/(1/E_w^0)$, was obtained from Figure 1. The E_w^0 value (43.2) represents the value of E_w at $\alpha = 1$ and is calculated from the nitrogen content of PEI. The curve of α vs. pH is shown in Figure 2, together with those

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