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Combined Chemical and Raman Spectroscopic Determination of Microstructural Arrangement in Poly(2,5-benzophenone)s

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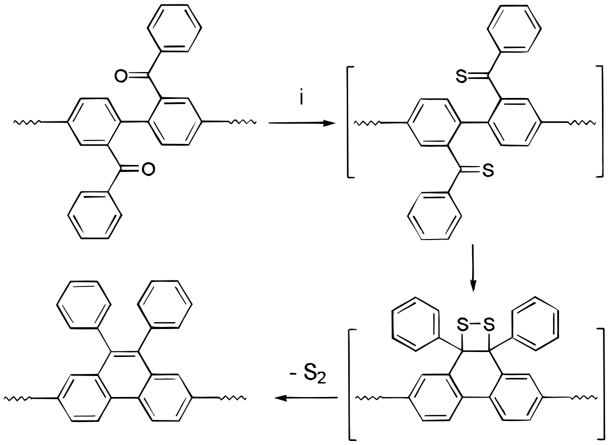
The Ni(0)-catalyzed couplings of aromatic dihalides are example reactions utilized for producing soluble polyarylenes.[1−3] This type of synthetic approach was first outlined by Colon and Kelsey for the synthesis of biphenyls.[4] Since then, many researchers have utilized this coupling reaction to synthesize polyarylenes from bis(aryl chloride)s.[5−8] Poly(2,5-benzophenone) (PBP) is a member of a new class of rigid-rod, high strength and modulus polyarylenes, which have a commercial potential as self-reinforced, high-performance materials.[9] PBP is typically synthesized from 2,5-dichlorobenzophenone in the presence of zinc, $NiCl_2$, and triphenylphosphine with or without coligand 2,2′-bipyridine in DMF or DMAc.[3,6,8,10] These PBPs typically display a glass transition temperature in the range 160−240 °C and a high Young's modulus over 10 GPa.[3,8,10] In a previous report,[10] two PBPs were made in the presence and absence of the bipyridine coligand and displayed different properties such as solubility, UV absorbance, and glass transition temperature. On the basis of these results, it was postulated that the two polymers have different structural regularities in the placement of the lateral benzoyl groups along the polymer backbone as a result of the ligand effect. Thus, it is believed that such subtle differences in a polymer's microstructure may give rise to larger differences in the mechanical properties of that polymer. Further in this regard, many other polyarylenes structurally analogous to PBP should behave similarly.

By fully understanding the structure−property relationship, it is possible that one may synthesize a PBP-like polyarylene with the desired properties, such as glass transition temperature and modulus, through manipulation of its microstructure. However, direct detection, such as NMR (^{1}H and ^{13}C) and IR spectroscopic methods, have so far proved futile in determination of the microstructures of poly(2,5-benzophenone)s,[5,10] due to poorly resolved signals of the important functional groups (e.g., carbonyl peaks). Clearly, other analytical methods and approaches need to be investigated.

We previously reported a chemo- and regiospecific, controlled intramolecular cyclization reaction (or deoxyolefination) which converts the 2,2′-dibenzoylbiphenyl moiety in a polymer into the phenanthrene unit (Scheme 1).[11] This transformation reaction proceeds rapidly in quantitative yield via a dithioketone intermediate as outlined previously. Since the 2,2′-dibenzoylbiphenyl moiety is also present in PBP, it is proposed that this unique chemical transformation, in combination with an appropriate spectroscopic method, may provide a new, general approach to determining the microstructures of PBP and its analogues. Considering a diad in repeating units in PBP, there are three possible arrangements as shown in Scheme 2: head-to-head (HH), head-to-tail (HT), and tail-to-tail (TT). For this intramolecular deoxyolefination to successfully occur, it is evident from the previous study that the HH arrangement is necessary between two given monomers.[11] Furthermore, it is important to note that a TT diad is equal to a HH diad since for a given infinite length both diads will yield the same phenanthrene unit after cyclization. Therefore, by carrying out this transformation, all the HH and TT diads should be converted into the phenanthrene units. Spectroscopic quantification should give the relative amount of phenanthrene units in the transformed polymers, which allows for calculation of the relative ratio or percentage of the HT diads to the sum of the HH and TT diads in PBP.

Scheme 1. Transformation of 2,2′-Dibenzoylbiphenyl into Diphenylphenanthrene Unit in Polymer (i, Lawesson's Reagent, TCE, Reflux)[11]



Scheme 2. Transformation on All Possible Diads in PBP (i, Lawesson's Reagent, TCE, Reflux, 18 h)

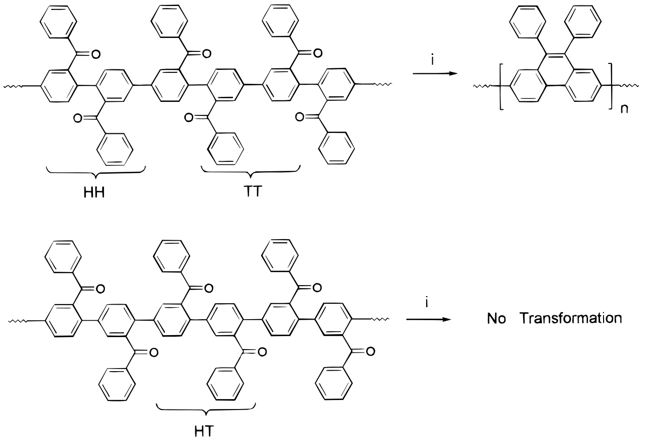


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Table 1. Characteristics of PBP-1 and PBP-2

characteristic	PBP-1[a]	PBP-2[b]
T_g (°C)[c]	154	234
T_d (°C)[d]	517	513
λ_{max} (nm)[e]	327	356
M_w[f]	239000	43400
M_n[f]	106000	25500
M_w/M_n	2.26	1.71
HT (%)	87.7	71.2
HH, TT (%)	12.3	28.8

[a] Without the use of 2,2′-bipyridine as coligand in polymerization. [b] With the use of 2,2′-bipyridine as coligand in polymerization. [c] From second run of oscillating DSC (Seiko DSC 220C with a heating rate of 1 °C/min). [d] Onset temperature for 5% weight loss in nitrogen at a heating rate of 10 °C/min. [e] In chloroform solution. [f] Values obtained by GPC analysis relative to polystyrene standards.

We report herein an investigation into the microstructures of two representative poly(2,5-benzophenone)s, PBP-1 and PBP-2 prepared in absence and the presence of 2,2′-bipyridine, respectively. This was done by utilizing the described intramolecular transformation reaction in combination with the FT-Raman spectroscopic quantification of the resulting phenanthrene units in the polymer backbone.

The Ni(0)-catalyzed polymerization of 2,5-dichlorobenzophenone was carried out as previously described[10] to yield both PBP-1 (without bipyridine coligand) and PBP-2 (with bipyridine ligand). The polymer characteristics (Table 1) are in good agreement with those published before.[10] However, the glass transition temperatures were found to be 154 and 234 °C for PBP-1 and PBP-2, respectively, using DSC in the oscillating mode.

According to a known procedure,[11] treatment of PBP-1 and PBP-2 with an excess of Lawesson's reagent (ca. 2 mol equiv) over a long period of time (ca. 18 h) in refluxing 1,1,2,2-tetrachloroethane (TCE), followed by hydrolysis of the unreacted thioketone back to the ketone, afforded the transformed polymers (TPBP-1 and TPBP-2). The reaction conditions and extensive washing with acetone in a Soxhlet extractor assured the complete conversion of all the 2,2′-dibenzoylbiphenyl units in the parent polymers and the composition of the ketone and phenanthrene groups in the transformed polymers. TPBP-1 and TPBP-2 were found to be extremely insoluble. They displayed a higher thermal stability than the parent polymers, as assessed by thermogravimetry, and had the onset temperatures of 537 and 522 °C for 5% weight loss in nitrogen for TPBP-1 and TPBP-2, respectively. The transformed polymers were first examined using IR spectroscopy. The IR spectra displayed the peaks for phenanthrene that were not significantly different from those seen in the parent polymer to allow for a clear quantification. In contrast, the Raman spectrum of phenanthrene shows a unique peak at approximately 1350 cm^{-1} that is not evident in PBP. Accordingly, TPBP-1 and TPBP-2 were analyzed by FT-Raman spectroscopy. Both spectra displayed the presence of the phenanthrene peak at 1350 cm^{-1} and the carbonyl peak at 1603 cm^{-1}.

By using phenanthrene as an internal standard, a calibration curve was constructed (Figure 1). The graph displays a ratio for the peak area of phenanthrene (1350 cm^{-1}) to the peak area of the carbonyl group (1603 cm^{-1}) over a series of PBP-1 and phenanthrene mixtures. Thin films were cast from the solution of polymer−phenanthrene mixtures (15 mg in total for each mixture) in chloroform and used for Raman measurement (standard 1.06 mm excitation). The calibration curve in Figure 1 displays good agreement between the plotted points, having an R^2 value of 0.9938. The equation of the line was determined to be $Y = -0.8161X + 73.08$, where Y is equivalent to a ratio of phenanthrene units to unreacted carbonyl groups in TPBP and X ($0 < X < 100\%$) is equivalent to the percentage of the remaining portion or HT diads in PBP.

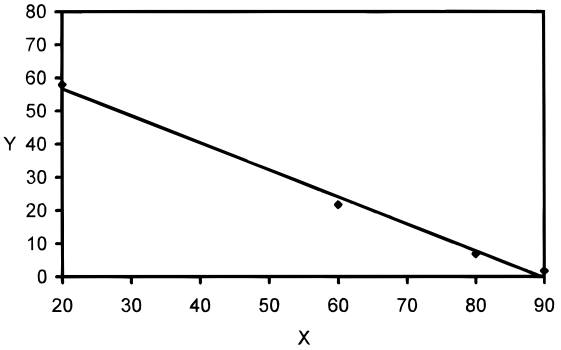

Figure 1. Calibration curve for transformation of PBP. Y = ratio of phenanthrene to carbonyl group in TPBP; X = percentage of HT diads in PBP.

The peak area ratios (Y) of phenanthrene to carbonyl groups in the transformed polymers from their Raman spectra were found to be 1.5 and 15 for TPBP-1 and TPBP-2, respectively. Substitution of these values into the determined line equation yields a percentage (X) of the HT diads for PBP-1 and PBP-2 as 87.7% and 71.2%, respectively. This indicates that the polymerization in the presence of a bipyridine coligand produces a PBP with less HT arrangement than the one without bipyridine.

Even though the polymer characteristics are in good agreement with those reported earlier,[10] our results are opposite to a previous conclusion proposed on the microstructures of PBP-1 and PBP-2. Earlier work suggested that PBP-2 would have a more regular structure (i.e., more HT association) than PBP-1 based on the fact that PBP-2 has a higher absorption maximum and thus likely contains a more conjugated segment.[10] It is possible that not all HH/TT arrangements will be "out of plane" as was earlier suggested. Looking at the TT arrangement (Scheme 2), the benzoyl groups could be opposite in plane with one and other, which would still allow for the extended π-conjugation along the main chain. Thus, even though PBP-2 displays a higher UV absorption maximum, it does not necessarily infer that there is more HT arrangement than in PBP-1.

Others[10] and we observed that PBP prepared with bipyridine has a higher T_g than the one prepared without bipyridine. The difference in T_g value is more than 50 °C. We previously showed that the poly(aryl ether)s containing the 2,2′-dibenzoylbiphenyl moiety have higher T_g values than those containing the 3,3′-dibenzoylbiphenyl moiety.[12] In PBP, each of the HH and TT diads is indeed represented by the 2,2′-dibenzoylbiphenyl moiety, and the HT unit is equivalent to the 3,3′-dibenzoylbiphenyl moiety. Therefore, the more HH/TT diads, the higher the T_g value. In this work, PBP-2 had about 30% of HH and TT diads and PBP-1 had only 12% of HH and TT diads. The former had a T_g of 234 °C, 80 °C higher than the latter.

In conclusion, we have demonstrated a unique method for easy and accurate determination of a portion of the microstructural arrangement, specifically the amount of HT diads, in PBP and also possibly in other polyarylenes structurally analogous to PBP. The use of 2,2′-bipyridine in polymerization results in the formation of PBP and analogous polymers with fewer HT diads. As well, the chemical transformation reaction can be applied to a variety of PBP-like polymers, to change the polymer properties such as thermal stability, glass transition temperature, and solvent resistance. It is also conceivable to establish a direct correlation between the T_g value of PBP and its microstructure (e.g., HT diad).

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