Carbon-13 Nuclear Magnetic Resonance of 2,4,6-Tribromoheptane. Chemical Shifts of the Diastereoisomers as Models of Poly(vinyl bromide)

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ABSTRACT: A mixture of the three diastereoisomers of 2,4,6-tribromoheptane has been prepared and examined in a variety of solvents by ^{13}C NMR. At 50.3 MHz, spectra of poly(vinyl bromide) show well-resolved methylene carbon tetrad and methine carbon pentad splittings. These have been assigned definitively to stereosequences in accord with the model compound data. The conformationally averaged γ effects of Br on the chemical shift of a CHBr carbon and of a CHBr carbon on the chemical shift of a CH_2 carbon are −2.6 and −1.8 ppm, respectively.

In a previous publication[1] we examined the tacticity of poly(vinyl bromide) (PVB) by ^{13}C NMR spectroscopy. The stereochemical assignments reported therein were based on chemical shifts observed for 2,4-dibromopentane (DBP), even though it was recognized that this compound is not a definitive model for PVB.

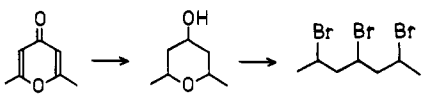
Recent work by Tonelli et al.[2] has led to a consistent interpretation of conformational influences on stereochemical shifts in the ^{13}C resonance patterns from vinyl homopolymers via a three-bond, gauche-effect model.[3] This model requires a conformational analysis of the polymer by rotational isomeric state (RIS) theory and knowledge of the "γ-effect" parameters $\gamma_{X,Y}$ ($\gamma_{X,Y}$ is the perturbation in chemical shift of nucleus X after a bond rotation which brings the γ substituent Y, i.e., the atom removed by three bonds, from the trans into a gauche arrangement).

The above model has not been successful to date in describing the ^{13}C NMR spectrum of PVB.[4] This failure is attributable to the present uncertainty in the RIS model for PVB, uncertainty in the values for $\gamma_{CH,Br}$ and $\gamma_{CH_2,CHBr}$, and uncertainty in assignments of the PVB methylene or CH_2 carbon stereosequences, which have relative chemical shifts strongly dependent on solvent.

In order to shed some light on these uncertainities, we have prepared a mixture of diastereoisomers of 2,4,6-tribromoheptane (TBH) which model the isotactic (I), heterotactic (H), and syndiotactic (S) stereosequences in PVB. We report here the complete ^{13}C chemical shift assignments for each isomer in a variety of solvents, as well as new data for *meso*- and *rac*-DBP under comparable conditions. We also report ^{13}C NMR spectra of PVB at 47 kG which show a substantial improvement over previously published spectra and which allow more detailed assignments.

Experimental Section

Materials. The 2,4-dibromopentane used in this work has been described previously.[1] 2,4,6-Tribromoheptane was synthesized according to the procedure outlined by Overberger and Scheinfeld:[5]



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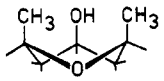
Twenty-five grams of 2,6-dimethylpyran-4-one (I) (Aldrich Chemical Co., 99% pure) was dissolved in 250 mL of absolute ethanol. The solution was placed in a Parr low-pressure, shaker-type hydrogenation apparatus to which 12 g of activated catalyst (5% Pt powder on carbon, Alfa Division, Ventron Corp.) had been added. Hydrogenation was carried out at 55 °C under 4-atm hydrogen pressure for 6 days. The extent of hydrogenation was followed with ^1H NMR by monitoring the decrease in the unsaturated resonance at 6 ppm.

The product was recovered by filtering the ethanol solution through Celite, after which the ethanol was removed under vacuum on a rotary evaporator. The residue was distilled at 10-mmHg pressure, and the fraction condensing between 68 and 70 °C was further purified by preparative liquid chromatography on a silica gel column with 30:70 ethyl acetate–hexane as the solvent.

The yield was 7.4 g (28%) of 2,6-dimethyl-4-hydroxytetrahydropyran (II), with a purity exceeding 95% according to NMR analysis. The three possible stereoisomers were obtained in an approximate 57:26:17 ratio, and the major fraction collected after liquid chromatography was most likely the all-cis isomer, which is expected under the hydrogenation conditions.



cis,cis,cis-II

Its ^1H NMR spectrum at 200 MHz was too complex for a straightforward analysis to confirm this isomeric form. The ^{13}C NMR spectrum at 50.3 MHz for a solution in $CDCl_3$ at 20 °C, with internal Me_4Si reference, was assigned as follows: $\delta(CH_3)$, 21.75; $\delta(CH_2)$, 42.55; δ(CHOH), 67.66; δ(OCHMe), 71.53.

Hydrogen bromide (Matheson Gas Products, 99.8%) was bubbled through 7.4 g of the pure 2,6-dimethyl-4-hydroxytetrahydropyran in 25 mL of glacial acetic acid at 100 °C for 20 h. The resulting brown oil was taken up in diethyl ether and washed in a separatory funnel with aqueous sodium bicarbonate and water. The ether extract was dried over calcium chloride and distilled under reduced pressure. The brown, oily residue was eluted through acidic alumina with hexane and subjected to fractional distillation, with hydroquinone added as a stabilizer. The fraction condensing between 92 and 97 °C at 3-mmHg pressure was collected. The yield was 9 g (47%) of 2,4,6-tribromoheptane (III) with a purity of 97%. The only impurity detected by NMR appeared to be 2,6-dimethyl-4-bromotetrahydropyran.

Separation of the TBH mixture into its three diastereoisomers was attempted by liquid and gas chromatography without success. The diastereoisomers did not separate under the liquid chromatography conditions used for the tetrahydropyran derivative, and fractions collected by "peak shaving" differed slightly in their diastereoisomer ratio. Separation was better by gas chromatography on a Varian Aerograph 90-P instrument (using conditions developed to obtain the pure stereoisomers of 2,4-DBP), but TBH was too unstable at the high injection port temperature (285 °C) necessary for volatilization and the yield of undegraded material was negligible.

The PVB used in the present study was prepared at 33 °C by exposing pure liquid monomer to a total of 0.21 Mrad of ^{60}Co γ radiation. The conversion of monomer to polymer was 30%.

Methods. NMR spectra were recorded at 47 kG on a Varian XL-200 spectrometer (200 MHz for ^1H, 50.3 MHz for ^{13}C). The

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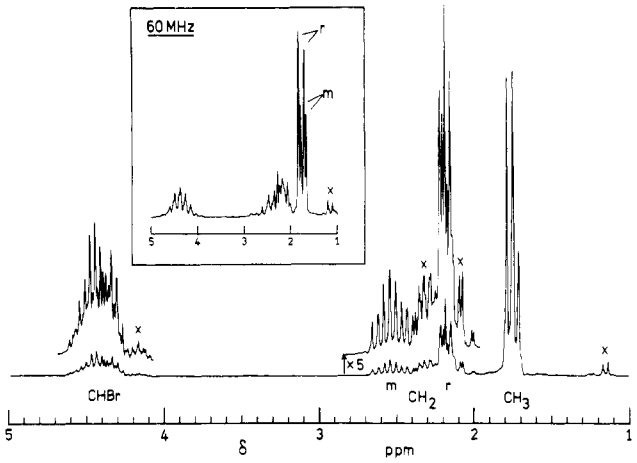


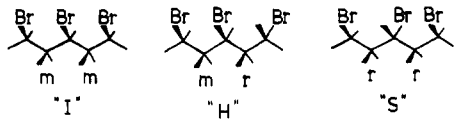
Figure 1. 200-MHz ^{1}H NMR spectrum of the mixture of TBH diastereoisomers dissolved in methylene-d_2 chloride at 18 °C (X = impurity peaks). The sample observed at 60 MHz is shown in the inset.

chemical shift reference was internal Me_4Si (δ 0.00) in all cases. The TBH solutions were placed in 10-mm sample tubes for ^{13}C NMR spectra, which were acquired under the following conditions: 50 transients were stored in 32 K computer locations, with a sweep width of 8000 Hz (2.0-s acquisition time) and a 10.0-s delay between 90° pulses (14.0-μs pulse width).

The resonances observed for DBP were assigned to their respective carbons according to previous procedures.[1] Assignments for TBH spectra were not so straightforward, owing to extensive overlap of resonances from the 2,6-CHBr and CH_2 carbons. In some cases proton-coupled ^{13}C NMR spectra were recorded for assignment purposes; the multiplicities and $^1J_{^{13}C-^1H}$ values in Hz were as follows: CH_3, quartet, 128; CH_2, triplet, 130; CHBr, doublet, 154. In other cases where the proton-coupled spectrum was too complex owing to overlap, assignments were made by comparing proton-decoupled spectra recorded with pulse intervals of 2 and 60 s. The CHBr carbons are saturated more readily than the CH_2 carbons, owing to their longer spin–lattice relaxation times, so their resonance intensities are decreased relative to those for CH_2 carbons at the shorter pulse interval.

Results and Discussion

Stereoprojections of the all-trans conformers of the three diastereoisomers of TBH are shown below:



These may be differentiated readily according to the ^{1}H NMR spectra exhibited by their methylene groups.[6]

Figure 1 shows ^{1}H NMR spectra at 60 and 200 MHz of TBH obtained by the procedure described in the previous section. Methylene protons within meso (m) dyads are more nonequivalent than those within racemic (r) dyads. The former are responsible for the multiplet centered at 2.54 ppm, whereas the latter give a simpler triplet centered at 2.18 ppm. The relative areas under these multiplets show that r dyads predominate.

The methyl resonances are likewise sensitive to only their immediate dyad environment and appear as a doublet of doublets ($J \sim 6.6$ Hz) centered at 1.76 and 1.72 ppm when observed at 60 MHz. The fortuitous overlap observed at 200 MHz results in an apparent triplet. On the basis of the methylene proton resonance intensities, the more intense low-field doublet must correspond to the r dyad environment, and the less intense high-field doublet must correspond to the m dyad environment. These assignments agree well with the methyl proton shifts of 1.78 and 1.72 ppm reported for *rac*- and *meso*-DBP, respectively.[7]

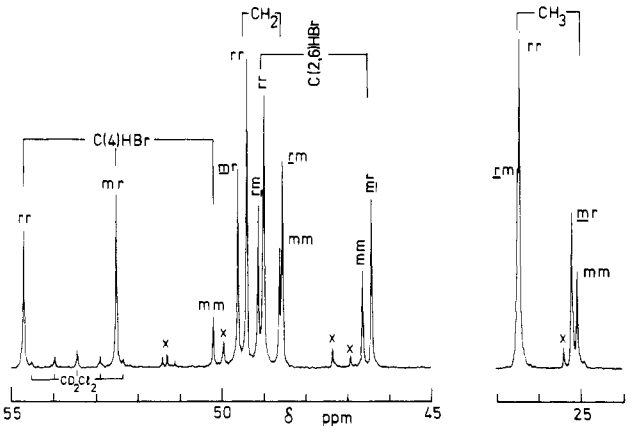


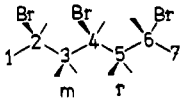
Figure 2. 50.3-MHz ^{13}C NMR spectrum of the mixture of TBH diastereoisomers in methylene-d_2 chloride at 20 °C (X = impurity peaks). For details of the notation and assignment procedures see main text.

It is clear from the ^{1}H NMR spectrum that the TBH sample is a mixture of the three diastereoisomers. The methyl resonances indicate an r/m ratio of 1.63. However, the I:H:S ratio cannot be determined by ^{1}H NMR, but it is readily obtained by ^{13}C NMR, as described in the following.

The 50.3-MHz ^{13}C NMR spectrum of the TBH mixture in methylene-d_2 chloride is shown in Figure 2. There are 15 separate resonances. Each carbon is split into four resonances depending on the relative stereochemistry within each isomer, except for the C(4) methine carbon, which is centrosymmetric and has only one resonance from the heterotactic isomer. The C(4)HBr resonance is a triplet (centered at 52.5 ppm, with a spacing of ca. 2.2 ppm), corresponding to S, H, and I diastereoisomers, in order of increasing field.

The above assignments follow from ^{1}H NMR results which gave an r/m dyad ratio greater than unity, so the S/I diastereoisomer ratio must necessarily exceed unity also. For example, with the assignments given in Figure 2, the following diastereoisomer proportions are obtained from C(4)HBr resonance intensities: S:H:I = 38:48:14. These figures are consistent with an r/m ratio of 1.63, which is in exact agreement with the ratio obtained from ^{1}H NMR spectra.

The quartets observed for each of the CH_2, C(2,6)HBr, and CH_3 carbons were assigned as follows. The most and least intense peaks within each quartet must be rr (S) and mm (I), respectively, according to the above diastereoisomer proportions. However, the two nonequivalent resonances in each quartet from the H isomer must, in principle, have equal intensities.[8] They were assigned by inspection of their chemical shift differences from the rr and mm resonances and by consideration of three-bond gauche interactions as exemplified below.



The CH_3 carbons have C(4) as their γ substituent. The likelihood of C(1) being gauche to C(4) depends on the C(2)–C(3) bond rotation probability, which in turn depends more on the relative stereochemical relationship between C(2)–C(4) (e.g., m) than that between C(4)–C(6) (e.g., r). Therfore the chemical shift of C(1) ought to be more sensitive to the identity of the closer dyad (*m*) than that

of the farther dyad (r),[9] if the gauche effect is the primary mechanism for differences in stereoisomer chemical shifts. It follows that the absolute chemical shift differences $\Delta(mr - mm)$ and $\Delta(rm - rr)$ should be substantially less than $\Delta(mr - rr)$ and $\Delta(rm - mm)$, so the *rm* and *mr* assignments follow by inspection once the rr and mm positions have been established.

Similar considerations apply to the C(2)HBr resonances, where the frequency of gauche contacts of C(2) with C(5) depends on C(3)–C(4) bond rotation probabilities. It turns out, however, for C(3) that its gauche interactions with C(6) depend more on the identity of its neighboring dyad than that of its surrounding dyad, since C(4)–C(5) bond rotations are involved. The relative magnitudes of the absolute splittings are reversed for C(3) as a result, with $\Delta(mr - mm)$ and $\Delta(rm - rr)$ being greater than $\Delta(mr - rr)$ and $\Delta(rm - mm)$.

The completed assignments for TBH in several solvents and the comparable data for DBP are shown in Table I. Several features of these data are interesting.

The magnitudes of $\Delta(r - m)$ for the CH_3, CHBr, and CH_2 carbons of DBP agree very closely with the corresponding $\Delta(rm - mm)$ and $\Delta(rr - mr)$ values for the CH_3, C(2,6)HBr, and CH_2 carbons of TBH under identical observation conditions. This fact supports the gauche effect argument used above to assign the heterotactic resonances. Furthermore, the absolute δ values for the CH_3 and CHBr carbons in *meso*- and *rac*-DBP are very close to those for the CH_3 and C(2,6)HBr carbons of TBH with the corresponding local dyad structure. The sterochemical assignments are therefore self-consistent, and the conformationally averaged values $\bar{\gamma}_{CHBr,CH_3}$ (in DBP) and $\bar{\gamma}_{C(2,6)HBr,CH_2}$ (in TBH) must not be substantially different (the bar above γ is used to denote this average). The difference in chemical shifts of methylene carbons in comparable local dyad structures of TBH and DBP, $\delta(CH_2,TBH) - \delta(CH_2,DBP)$, reflects the value of $\bar{\gamma}_{CH_2,CHBr}$, i.e., ca. −1.8 ppm.

The value of $\bar{\gamma}_{CHBr,Br}$ can be estimated by comparing the present data with the chemical shifts of 4-bromoheptane. We obtained the following δ values for 4-bromoheptane in chloroform: C(1), 13.47; C(2), 20.89; C(3), 41.49; C(4), 57.85. The C(4) carbon has two γ Br substituents in TBH and none in 4-bromoheptane. It follows that $\bar{\gamma}_{CHBr,Br}$ is about −2.6 ppm if the γ effect is linearly additive.

It should be stressed that the above $\bar{\gamma}$ values may be substantially different from the corresponding nonaveraged γ values because the populations of rotational states about the relevant bonds can differ from one model (e.g., TBH) to the next (e.g., DBP). The applicable γ parameters can be derived only after an RIS treatment of the molecule in question.[3]

The influence of solvent on the chemical shifts from TBH is illustrated in Figure 3. In an absolute sense the methyl carbons are the least sensitive, whereas the brominated carbons are the most sensitive. However, the relative chemical shifts within each individual resonance pattern for these carbons change very little compared to their overall dispersion from stereoisomerism. In contrast, the methylene resonances shift significantly with respect to each other with different solvents, and certain lines coalesce or cross over, depending on the observation conditions. Similar changes occur in ^{13}C NMR spectra of PVB, where the overall appearance of the methylene region can change from one solvent to the next.[1]

Small temperature differences (up to 50 °C) do not have as pronounced an influence on TBH spectra as solvent differences (Table I). The difference in chemical shift

Table I
^{13}C δ Values (±0.02, $Me_4Si \equiv 0.00$) for the Diastereoisomers of 2,4,6-Tribromoheptane and 2,4-Dibromopentane

		2,4,6-TBH														2,4-DBP					
		C(4)HBr			C(2,6)HBr			CH_2			CH_3			CHBr		CH_2		CH_3	
solvent	temp, °C	S rr	H mr	I mm	H rm	S rr	I mm	H′ mr	H′ mr	S rr	I mm	H rm	S rr	H′ mr	I mm	r	m	r	m	r	m
neat	23	54.19	52.06	49.84	48.59	48.48	46.16	45.93	49.14	48.94	48.13	48.02	26.26	26.23	25.03	24.85	49.16	46.64	51.06	51.06	26.35	25.26
cyclohexane	20	54.15	52.15	50.37	48.21	47.96	45.89	45.45	50.30	50.30	49.14	49.50	26.65	26.62	25.22	25.25	49.01	46.46	52.00	51.89	26.61	25.49
dioxane	23	55.04	53.05	50.83	49.46	49.23	47.15	46.78	49.80	49.57	48.86	48.79	26.43	26.38	25.07	25.03	50.03	47.52	51.43	51.50	26.42	25.32
dioxane	69	54.46	52.65	50.50	49.05	48.74	46.78	46.42	50.07	49.97	49.10	49.25	26.44	26.38	25.19	25.17						
tetrahydrofuran	23	55.30	53.20	51.00	49.57	49.39	47.17	46.88	50.18	49.86	49.25	48.94	26.58	26.55	25.34	25.17	49.83	47.34	51.59	51.70	26.50	25.42
tetrahydrofuran	50	54.59	52.60	50.42	49.00	48.76	46.61	46.31	50.04	49.85	49.05	48.97	26.50	26.45	25.29	25.17						
methylene chloride	20	54.66	52.49	50.18	49.11	48.99	46.62	46.40	49.60	49.40	48.60	48.53	26.47	26.45	25.19	25.07	49.90	47.30	51.42	51.50	26.52	25.44
dimethyl sulfoxide	23	55.74	53.45	51.40	50.43	50.36	47.87	47.95	48.96	48.24	48.24	47.15	26.16	26.10	25.26	24.80	50.41	48.08	50.56	50.94	26.20	25.22
dimethyl sulfoxide	50	55.46	53.29	51.25	50.23	50.14	47.78	47.78	49.15	48.54	48.46	47.55	26.19	26.12	25.30	24.92						

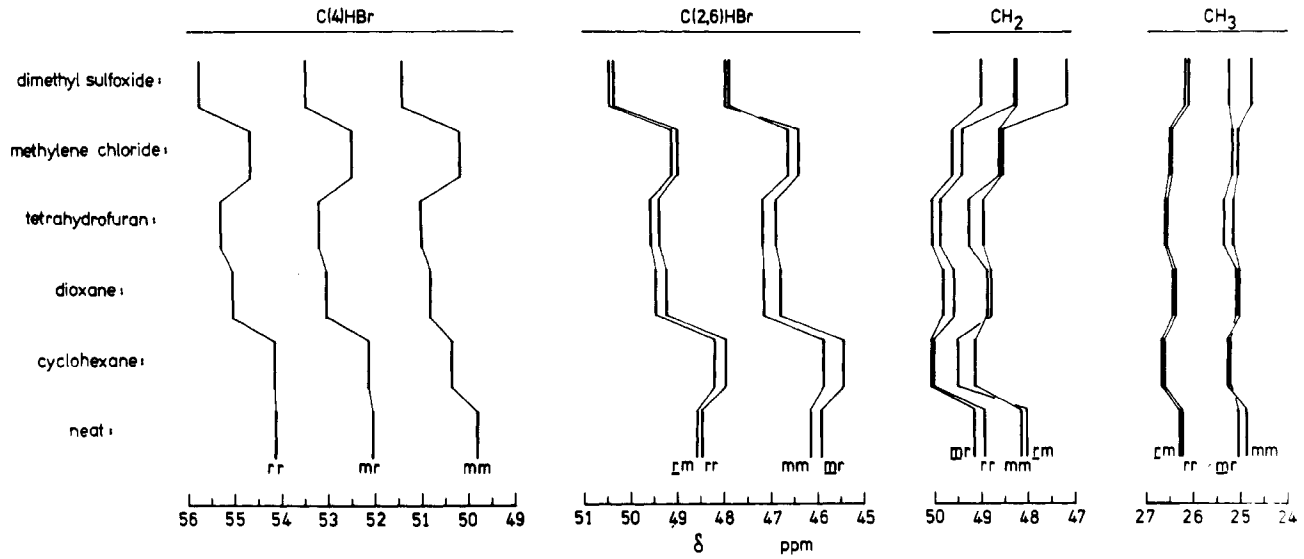


Figure 3. Schematic representation of the effect of solvent on the ^{13}C NMR chemical shifts of TBH.

between different stereoisomers is reduced slightly for each chemically distinct carbon with an increase in temperature.

The ^{13}C NMR spectra of PVB can now be analyzed more confidently with the new TBH data presented here. Figure 4 shows the 50.3-MHz spectrum of PVB in tetrahydrofuran. The general features resolved at lower field have been described previously.[1] We have since tested more solvents and found that tetrahydrofuran results in a good separation of methine and methylene carbon resonance regions (49.5–54.5 and 45.5–49.0 ppm, respectively), and a good separation of methylene carbon stereosequence tetrads.

The C(4)HBr carbon in TBH is an excellent model for the major triad splitting of the methine carbon in PVB. The data in Table I confirm our previous assignments for this region.[1] All ten stereosequence pentads are resolved in Figure 4, and the assignments shown at this level are based on intensities from Bernoullian statistics with a P_m value of 0.46, which was derived in turn from the three triad peak areas and their established assignments. The only pentad assignments we cannot make unambiguously are for the equally intense mmrr and rmrm peaks; their order of assignment in Figure 4 may be interchanged.

The CH_2 resonances from TBH provide some new insight into the PVB spectrum, even though the models do not precisely mimic tetrad stereosequences. The chemical shifts in Table I show that the CH_2 resonance is more sensitive to the identity of the neighboring dyad than that in which the observed carbon is centered. Furthermore, an r dyad neighbor deshields more than an m dyad neighbor, and an m-centered dyad is usually less shielded than an r-centered dyad. These observations predict a triplet of doublets for the CH_2 resonance in PVB, with the following order of stereosequence tetrads from low to high field: (rmr, rrr), (rmm, rrm), and (mmm, mrm). The smaller doublet splitting between sequences within each set of parentheses reflects differences in the center dyad (i.e., m vs. r). The large triplet splitting between sequences within one set of parentheses and the next reflects differences in the neighboring dyad combinations (i.e., rr vs. rm vs. mm).

The observed PVB spectrum (Figure 4) is consistent with the above predictions. The methylene carbon resonance assignments were made by matching observed intensities with those calculated as described above. These assignments were verified by comparison with a spectrum of PVB which had a different P_m value.[1] Five of the six

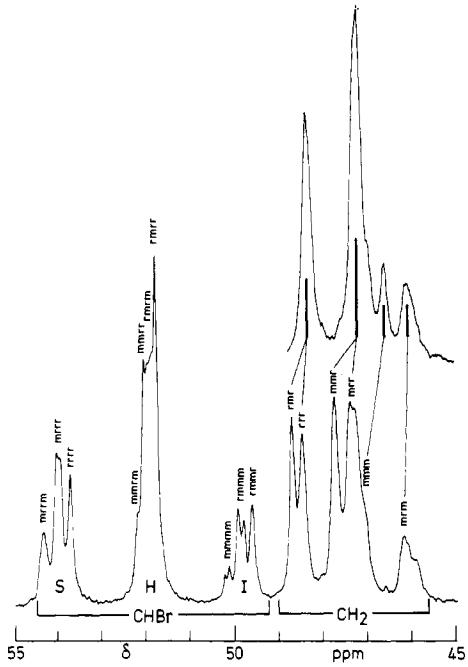


Figure 4. 50.3-MHz ^{13}C NMR spectrum of PVB in tetrahydrofuran-d_8 at 50 °C (lower full trace). The upper trace shows the methylene carbon region only for the same polymer in methylene-d_2 chloride at 45 °C. The major triplet splitting of the methine carbon region corresponds to S-, H-, and I-centered stereosequences.

tetrads are fully resolved in tetrahydrofuran. The mmm resonance occurs as a shoulder on the more intense mrr resonance, but it can be resolved in methylene chloride solution, as shown by the upper trace in Figure 4. It is interesting that the doublet splitting between m- and r-centered sequences with rr neighbors, as well as those with mr neighbors, cannot be resolved in methylene chloride solutions, so that the spectrum of the methylene carbon of PVB appears deceptively simple in this solvent.

Conclusions

The diastereoisomers of TBH are realistic models for the stereosequences in PVB. Previous assignments made in the polymer spectrum on the basis of chemical shifts for *meso*- and *rac*-DBP have now been confirmed. The present results provide an extensive set of independent data which, when combined with appropriate RIS treat-

ments, will lead to a thorough understanding of bromine substituent effects in polymer ^{13}C NMR spectra. We will illustrate these effects in ethylene–vinyl bromide copolymers in a subsequent publication.

Acknowledgment. We are grateful to Drs. S. H. Bertz and J. W. Suggs for advice concerning the synthesis of TBH, to Dr. A. E. Tonelli for his interest in this work, and to Dr. G. Khanarian for studying the feasibility of separating the TBH diastereoisomers by gas chromatography.

References and Notes

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(8) In our spectra obtained with a 10-s pulse interval, the carbons associated with the m segment of the heterotactic isomer were sometimes slightly less intense than those associated with the r segment. This fact indicates that there is a stereochemical influence on the dynamic behavior of TBH insofar as it influences ^{13}C nuclear relaxation.
(9) A notation is adopted here in which the closer of the two dyads with respect to the carbon under consideration is italicized in the stereosequence designation (e.g., *mr*) so that the two nonequivalent heterotactic resonances from each of carbons 1, 2, and 3 (7, 6, and 5) may be distinguished.

Fourier Transform Infrared Studies of Polymer Blends. 6. Further Observations on the Poly(bisphenol A carbonate)–Poly(ϵ-caprolactone) System

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ABSTRACT: Preliminary Fourier transform infrared (FT IR) studies of poly(bisphenol A carbonate) (PC)–poly(ϵ-caprolactone) (PCL) polymer blends have been reported elsewhere. In this publication we present further results pertaining to this gordian polymer blend system. Blends of PC and PCL are compatible in the amorphous state and both polymers are capable of crystallization. Not only is the state of order of the two polymeric components in the blend a function of composition and temperature but it is also markedly dependent upon the method of film preparation. FT IR spectroscopy has been employed to study the variation of crystallinity of both components in the blend from films cast from different solvents and at different evaporation rates. The effect of exposure to acetone vapor of the polymer blend films has also been studied. Additionally, attempts have been made to obtain information concerning the origin, type, and relative strengths of polymer–solvent interactions from solution FT IR studies of PC in a variety of solvents. Finally, stepwise temperature studies of the PC–PCL blends have been performed. Polymer-induced crystallization of PC is readily observed and the results are considered in terms of the predicted T_g of the amorphous phase. The melting point of PCL in the blends may also be determined. Implications concerning the polymer–polymer interaction parameter are discussed.

Introduction

In a recent paper[1] we presented the results of a Fourier transform infrared (FT IR) study of the poly(bisphenol A carbonate) (PC)–poly(ϵ-caprolactone) (PCL) blend system. This is a complex blend of two polymers which are both capable of crystallization and are compatible in the amorphous state. Furthermore, the crystalline melting points (T_m) and glass transition temperatures (T_g) of the two polymers are significantly different. From our FT IR studies we were able to present evidence supporting the presence of specific chemical interactions between the two polymeric components in the amorphous state which were analogous to those previously reported for the PCL–poly(vinyl chloride) (PVC) system.[2] In addition, we demonstrated that we could readily observe the development of crystallinity in either or both of the polymeric components as a function of blend composition and sample preparation (i.e., solvent and polymer-induced crystallinity). In the absence of solvent effects, we further concluded from studies at ambient and elevated temperatures that the effective T_g of the amorphous phase was the overriding factor in the development of crystallinity in these blends.

Nonetheless, several important questions concerning the mechanism of solvent- and polymer-induced crystallization arose as a direct consequence of the above work. Thin films of PC and the PC–PCL blends cast from methylene chloride (MC) invariably gave materials in which the PC component was amorphous under the experimental conditions employed. Conversely, when these films were cast from tetrahydrofuran (THF), the PC component was invariably semicrystalline. However, we did not appreciate at this time just how sensitive experimental evaporation conditions were to the deveopment of PC crystallinity in the films. In considering possible causes of this phenomenon we postulated that solvent evaporation rate and effectiveness of the solvent to plasticize the polymer through complex formation might be two important factors. In this paper we present the results of evaporation rate studies, solution infrared experiments which might indicate the type and relative strength of interactions occurring between the polymer and solvent, and the effect of exposing the film to acetone vapor. Additionally, we present in-

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