

Determination of k_2 and k_{-2} :

$$d[B]/dt = k_1[A] - k_2[B] + k_{-2}[C] \quad (1')$$

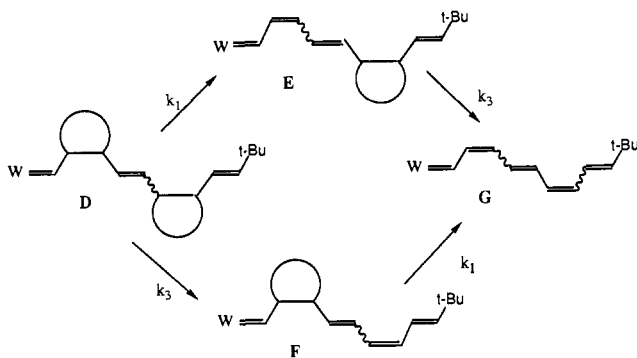
$$[C] = [A]_0 - [A] - [B] \quad (2')$$

Substituting $[A] = [A]_0 \exp(-k_1 t)$ and eq 2' into eq 1' and solving yield

$$[B] = [A]_0 \left[\frac{k_{-2}}{k_2 + k_{-2}} + \left\{ \frac{k_1 - k_{-2}}{k_2 + k_{-2} - k_1} \right\} \exp(-k_1 t) - \left\{ \frac{k_1 - k_{-2}}{k_2 + k_{-2} - k_1} + \frac{k_{-2}}{k_2 + k_{-2}} \right\} \exp[-(k_2 + k_{-2})t] \right]$$

If one sets $k_{-2} = k_2 K$ and uses $K = 0.294$, $k_1 = 6.5 \times 10^{-3} \text{ min}^{-1}$, $[A]_0 = 1.164$, and $[B]_{270} = 0.281$, one finds by graphical solution that $k_2 = 1.7 \times 10^{-2} \text{ min}^{-1}$ and hence $k_{-2} = 5.1 \times 10^{-3} \text{ min}^{-1}$.

To determine the rate of the retro-DA reaction in the second unit we will assume that two pathways to G are possible, viz.



For the sake of simplicity we will assume that the rates of the reactions $D \rightarrow E$ and $F \rightarrow G$ are identical and that the rates of the reactions $D \rightarrow F$ and $E \rightarrow G$ are identical. We will also assume that the rates of all retro reactions are independent of chain length, i.e., k_1 is the same in a precursor to 5 (D or F) as it is in a precursor to 3 (A).

Determination of k_3 :

$$[G] = [D]_0 - [D] - [E] - [F] \quad (3')$$

$$d[D]/dt = -k_1[D] - k_3[D] \quad \text{or} \quad [D] = [D]_0 \exp(-(k_1 + k_3)t) \quad (4')$$

$$d[E]/dt = k_1[D] - k_3[E] \quad (5')$$

$$d[F]/dt = k_3[D] - k_1[F] \quad (6')$$

Solving eq 5' and 6' gives eq 7' and 8':

$$[E] = [D]_0 \{ \exp(-k_3 t) \} (1 - \exp(-k_1 t)) \quad (7')$$

$$[F] = [D]_0 \{ \exp(-k_1 t) \} (1 - \exp(-k_3 t)) \quad (8')$$

Substituting eq 4', 7', and 8' into eq 3' and rewriting give

$$[G] = [D]_0 \{ 1 + \exp(-(k_1 + k_3)t) - \exp(k_1 t) - \exp(k_3 t) \} \quad (9')$$

Substituting $[G]_{270} = 0.2976$, $[D]_0 = 2.2815$, and $k_1 = 6.5 \times 10^{-3} \text{ min}^{-1}$ into eq 9' gives $k_3 = 6.3 \times 10^{-4} \text{ min}^{-1}$.

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Registry No. 1, 558-37-2; 2t₂, 22430-49-5; 3ct₂, 122093-75-8; 3t₃, 81380-18-9; 4ct₂, 122170-12-1; 4tct₂, 122170-13-2; 4t₄, 121987-85-7; 5tct₂, 122170-14-3; 5t₃t, 122170-15-4; 5tct₃, 122170-16-5; 5t₅, 121987-86-8; 6tctct₂, 122170-17-6; 6tctct₂, 122170-18-7; 6tctct₂, 122170-19-8; 6tct₄, 122170-20-1; 6t₆, 121987-87-9; 7t(ct)₃, 122170-21-2; 7tctct₃, 122170-22-3; 7tct₃ct, 122170-23-4; 7t₇, 121987-88-0; 8t₈, 121987-89-1; 9t(ct)₄, 122170-24-5; 9tctct₂ct, 122170-25-6; 9t(ct)₃t, 122170-26-7; 9tct₃ct, 122170-27-8; 9tct₇, 122170-28-9; 9t₉, 121987-90-4; 10t₁₀, 122093-76-9; 11t(ct)₅, 122093-77-0; 13t(ct)₆, 122093-78-1; 13t₁₃, 122170-29-0; 15t(ct)₇, 122093-79-2; (E)-t-BuCH=CHCHO, 22597-46-2; W(CH-t-Bu)(NC₆H₃-2,6-i-Pr₂)(O-t-Bu), 107440-84-6; pivaldehyde, 630-19-3; guaiazulene, 489-84-9.

Supplementary Material Available: Tables of proton NMR data for other identified polyenes and parameters for calculating carbon chemical shift in *all-trans*- or alternating polyenes (3 pages). Ordering information is given on any current masthead page.

Communications to the Editor

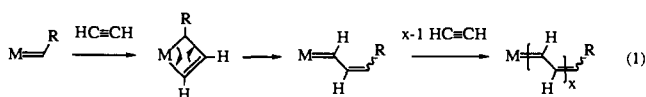
Direct Polymerization of Acetylene To Give Living Polyenes

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Polyacetylene has been of great interest in the past decade as (inter alia) a potential organic conductor,¹ but so far it has not been possible to prepare polyacetylene or shorter oligomers in a controlled polymerization of acetylene. There is good evidence that this should be possible under the right circumstances by using an alkylidene complex (eq 1).^{2,3} We report here the preparation of living polyenes of moderate length and block copolymers containing polyene sequences by this method.



Addition of up to 60 equiv of acetylene⁴ to a solution of W-(CH-t-Bu)(NAr)(O-t-Bu)₂ (Ar = 2,6-C₆H₃-i-Pr₂)⁵ in pentane yields a black, intractable precipitate of what appears to be a form of polyacetylene on the basis of its solid-state ¹³C NMR spectrum (broad singlet at 135 ppm).⁶ However, if W(CH-t-Bu)-

(1) (a) Chien, J. C. W. *Polyacetylene Chemistry, Physics and Material Science*; Academic Press: New York, 1984. (b) Skotheim, T. A., Ed. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986. (c) Kuzmany, H., Mehring, M., Roth, S., Eds. *Electronic Properties of Conjugated Polymers*; Springer Series in Solid State Sciences; Springer: New York, 1988; Vol. 76. (d) Bowden, M. J., Turner, S. R., Eds. *Electronic and Photonic Applications of Polymers. Adv. Chem. Ser. 1988, 218*. (e) Proceedings of the International Conference on the Physics and Chemistry of Low-Dimensional Synthetic Metals. In *Synth. Met. 1987, 17; Mol. Cryst. Liq. Cryst. 1985, 117, 118*. (f) Wegner, G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 361. (g) Baughman, R.; Bredas, J.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* **1982**, *82*, 209. (h) Simionescu, C. I.; Pereg, V. *Prog. Polym. Sci.* **1982**, *8*, 133. (i) Frommer, J.; Chance, R. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1986; p 462. (2) (a) Masuda, T.; Higashimura, T. *Adv. Polym. Sci.* **1986**, *81*, 121. (b) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422. (c) Han, C.-C.; Katz, T. J. *Organometallics* **1985**, *4*, 2186. (d) Katz, T. J.; Hacker, S. M.; Kendrick, R. D.; Yannoni, C. S. *J. Am. Chem. Soc.* **1985**, *107*, 2182. (e) Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737.

(3) Wallace, K. C.; Liu, A. H.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 644.

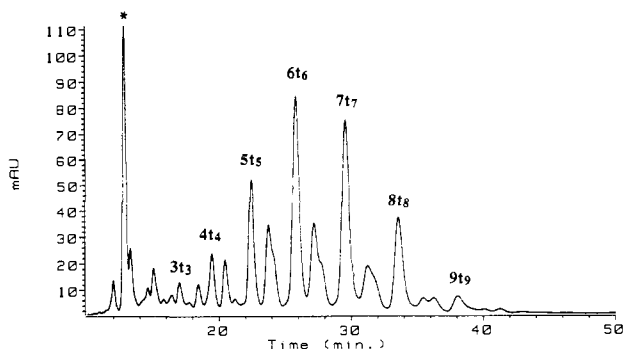


Figure 1. Reversed-phase HPLC study^{8b} of $(t\text{-Bu})(\text{CH}=\text{CH})_x(t\text{-Bu})$ prepared from $\text{W}(\text{CH-}t\text{-Bu})(\text{NAr})(\text{O-}t\text{-Bu})_2$, 5 equiv of $\text{HC}\equiv\text{CH}$ in the presence of 5 equiv of quinuclidine, and pivaldehyde in toluene (asterisk = guaiazulene internal standard).

$(\text{NAr})(\text{O-}t\text{-Bu})_2$ is treated with 3–13 equiv of acetylene in toluene in the presence of 5 equiv of quinuclidine, then yellow-to-red solutions are formed. Excess pivaldehyde was added to a red solution formed from 5 equiv of acetylene in order to cleave off the polyene chain in a Wittig-like reaction. HPLC analysis shows that an estimated total of ~65% of the di-*tert*-butyl-capped polyenes, $(t\text{-Bu})(\text{CH}=\text{CH})_x(t\text{-Bu})$ ($x = 3\text{--}9$; Figure 1) had been formed.^{7,8} The predominant polyenes are the all-trans forms, $3t_3$ (three double bonds), $4t_4$ (four double bonds, etc), $5t_5$, $6t_6$, $7t_7$, $8t_8$, and $9t_9$.^{8b} Other isomers of a given chain length that contain one or more cis double bonds elute before the all-trans form having that chain length.^{8b} (The percentage of all trans form varies from ~70% for $4t_4$ to ~60% for $8t_8$.) No other organic products, including benzene, could be detected by NMR (see below) or HPLC techniques. The most straightforward explanation of the role of quinuclidine is that it binds to a significantly greater extent to the metal in a living polyene oligomer, $\text{W}[(\text{CHCH})_x(\text{CH-}t\text{-Bu})](\text{NAr})(\text{O-}t\text{-Bu})_2$, than to $\text{W}(\text{CH-}t\text{-Bu})(\text{NAr})(\text{O-}t\text{-Bu})_2$ and thereby slows the rate of propagation significantly more than initiation.

Polyene sequences can be incorporated into triblock copolymers. If $\text{W}(\text{CH-}t\text{-Bu})(\text{NAr})(\text{O-}t\text{-Bu})_2$ (0.025 M in toluene) is treated with 50 equiv of norbornene (10-min reaction time), then 3–9 equiv of acetylene (10-min reaction time), and then 50 equiv of norbornene (10 min reaction time) and then capped by adding 10 equiv of benzaldehyde, triblock copolymers are obtained with molecular weights and polydispersities (Table I) that are similar to triblocks prepared by using 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene.⁹ If acetylene is omitted in the sequence (last entry in Table I), then the polynorbornene that is formed after cleavage with benzaldehyde is virtually identical with what is observed in the absence of quinuclidine.^{5b} The low polydispersities of the triblocks and M_n values that are virtually identical with those for 100 equiv of polynorbornene itself suggest that the polymerization of up to 9 equiv of acetylene is largely well-behaved. That is not true if 11 or (especially) 25 equiv of acetylene are employed in analogous experiments (Table I). A trimodal distribution is dominant in the latter experiment, the central peak of which (~25% of the total area) can be assigned to the expected triblock.

(4) All acetylene used in the experiments described here was purified by passing it through a column of activated alumina.

(5) (a) Schrock, R. R.; DePue, R.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423. (b) Schrock, R. R.; Feldman, J.; Grubbs, R. H.; Cannizzo, L. *Macromolecules* **1987**, *20*, 1169.

(6) (a) Maricq, M. M.; Waugh, J. S.; MacDiarmid, A. G.; Shirakawa, H.; Heeger, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 7729. (b) Gibson, H. W.; Pochan, J. M.; Kaplan, S. *J. Am. Chem. Soc.* **1981**, *103*, 4619. (c) Mehring, M.; Weber, H.; Miller, W.; Wegner, G. *Solid State Commun.* **1983**, *45*, 1079.

(7) Reaction conditions: 25 °C, 5 mg of catalyst in 1 mL of toluene, 30-min acetylene reaction time, 30-min quench reaction time with 10 equiv of pivaldehyde. See ref 8b for analytical HPLC procedures.

(8) (a) Knoll, K.; Krouse, S. A.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4424. (b) Knoll, K.; Schrock, R. R. *J. Am. Chem. Soc.*, preceding paper in this issue.

(9) Krouse, S. A.; Schrock, R. R. *Macromolecules* **1988**, *21*, 1885.

Table I. Polydispersities of Polynorbornene Triblocks Containing Polyene Blocks^a

NBE	$\text{HC}\equiv\text{CH}$	NBE	M_w	M_n	PDI
50	3	50	19 796	18 174	1.09
50	5	50	18 943	17 745	1.07
50	7	50	19 756	18 134	1.09
50	9	50	19 856	18 249	1.09
50	11	50	27 378	21 297	1.29
50	25	50	223 683	32 659	6.85
100			19 051	17 916	1.06

^a GPC data were obtained in dichloromethane vs polystyrene standards. The yield of polymer was quantitative. A single slightly unsymmetric peak was observed in all cases. (Catalyst concentration in toluene = 0.025 M.)

Low-temperature (down to -60 °C) ¹H NMR spectra of $\text{W}(\text{CH-}t\text{-Bu})(\text{NAr})(\text{O-}t\text{-Bu})_2$ in the presence of quinuclidine in toluene-*d*₈ show no evidence for a significant degree of adduct formation. However, the ¹H NMR spectrum of living polynorbornene prepared from $\text{W}(\text{CH-}t\text{-Bu})(\text{NAr})(\text{O-}t\text{-Bu})_2$ and 50 equiv of norbornene in toluene-*d*₈ in the presence of 5 equiv of quinuclidine shows a broad α -hydrogen resonance at 8.6 ppm instead of a well-defined doublet at 8.36 ppm.^{5b} When this sample is cooled to -40 °C, two doublet alkylidene H_α resonances are found at 9.72 and 8.97 ppm in a ratio of ~1:2, respectively. These resonances can be ascribed to two isomers that contain coordinated quinuclidine. (The low-temperature spectrum is unchanged if a total of 10 equiv of quinuclidine are added.) After addition of 5 equiv of acetylene to this sample of living polynorbornene at 25 °C, a spectrum recorded at -40 °C revealed a complex set of broad resonances between ~8.5 and ~11 ppm, but addition of another 50 equiv of norbornene at 25 °C yielded a sample whose NMR spectrum at -40 °C is identical with the initial spectrum, including the total intensity of the alkylidene resonances versus an internal standard. We conclude that quinuclidine partially binds to living polynorbornene at 25 °C and is exchanging rapidly on the NMR time scale, that the catalyst is still living after addition of 5 equiv of acetylene, and that living polynorbornene is regenerated upon addition of more norbornene. The complex set of resonances between ~11 and ~8.5 ppm have not yet been assigned, but we have shown that this is the region in which one finds H_α and H_β resonances in base adducts of well-characterized vinylalkylidene complexes that have two basic isomeric forms and *cis*- or *trans*-C_β-C_γ double bonds.¹⁰ These findings are also analogous to those obtained in NMR studies of living polyenes prepared indirectly by employing 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene.^{8b}

Preparation of polyene sequences from acetylene itself is the most direct method of preparing polyenes and "polyacetylene" in a controlled manner and is a viable alternative way to prepare polyenes via the controlled polymerization of 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene.^{8b} (Other ring-opening polymerization reactions that give polyacetylene have been reported,¹¹ but they have not yet been used to synthesize polyene oligomers.) We have shown that the analogous molybdenum catalyst¹² also yields living polyenes in what appears to be an even more controlled fashion (only bimodal distributions⁹) in the presence of quinuclidine.¹³ The fact that complexes of the type $\text{M}(\text{CH-}t\text{-Bu})(\text{NAr})(\text{O-}t\text{-Bu})_2$ are poor catalysts for the metathesis of ordinary internal olefins^{5,12} probably is a significant factor in channeling the reaction in the direction shown in eq 1 and in eliminating "backbiting" to form benzene.

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(10) Crowe, W. E., to be published.

(11) (a) Swager, T. M.; Dougherty, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2973. (b) Klavetter, F. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7807.

(12) Murdzek, J. S.; Schrock, R. R. *Macromolecules* **1987**, *20*, 2640.

(13) Stieglitz, S., unpublished results.

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Synthesis and Characterization of III-V Semiconductor Clusters: GaP in Zeolite Y

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Size quantization effects observed in small semiconductor clusters are currently of great interest for potential nonlinear optic and photocatalytic applications.¹⁻¹¹ While materials based on II-VI semiconductors have been extensively studied, the preparation of III-V size quantized semiconductors has been hampered by the much less-developed solution state chemistry in such systems.¹² With the use of inclusion chemistry, we have succeeded in preparing small clusters of GaP in a crystalline, periodic environment of well-defined size and shape (zeolite Y).

The reaction $(\text{Me})_3\text{Ga} + \text{PH}_3 \rightarrow 3\text{CH}_4 + \text{GaP}$ was carried out within the pores of Na⁺/H⁺ exchanged zeolite Y, by using various loadings of (Me)₃Ga and different reaction temperatures and times with PH₃. The synthesis is accomplished by vapor transfer of (Me)₃Ga into dry zeolite and slowly warming to room temperature, resulting in CH₄ evolution due to the reaction of (Me)₃Ga with Brønsted acid sites in the zeolite. Excess (Me)₃Ga and CH₄ are

- (1) Henglein, A. *Top. Curr. Chem.* **1988**, *143*, 113.
- (2) Brus, L. J. *Phys. Chem.* **1986**, *90*, 2555-2560.
- (3) Rajh, T.; Vucemilovic, M. I.; Dimitrijevic, N. M.; Micic, O. I.; Nozik, A. J. *Chem. Phys. Lett.* **1988**, *143*(3), 305-308.
- (4) Steigerwald, M. L.; Alivisatos, A. P.; Gibson, J. M.; Harris, T. D.; Kortan, R.; Muller, A. J.; Thayer, A. M.; Duncan, T. M.; Douglass, D. C.; Brus, L. E. *J. Am. Chem. Soc.* **1988**, *110*, 3046-3050.
- (5) Wang, Y.; Herron, N.; Mahler, W.; Suna, A. *J. Opt. Soc. Am. B.* **1989**, *6*, 808.
- (6) Herron, N.; Wang, Y.; Eddy, M. M.; Stucky, G. D.; Cox, D. E.; Moller, K.; Bein, T. *J. Am. Chem. Soc.* **1989**, *111*, 530-40.
- (7) Moller, K.; Eddy, M. M.; Stucky, G. D.; Herron, N.; Bein, T. *J. Am. Chem. Soc.* **1989**, *111*, 2564-2571.
- (8) Dameron, C. T.; Reese, R. N.; Mehra, R. K.; Kortan, A. R.; Carroll, P. J.; Steigerwald, M. L.; Brus, L. E.; Winge, D. R. *Nature* **1989**, *338*, 596-7.
- (9) Wang, Y.; Herron, N. *J. Phys. Chem.* **1987**, *91*, 257-260.
- (10) Henglein, A. *J. Chem. Phys.* **1987**, *84*(9), 1043-1047.
- (11) Grätzel, M. *Nature* **1989**, *338*, 540-541.
- (12) See, for example: Byrne, E. K.; Parkanyi, L.; Theopold, K. *Science* **1988**, *241*, 332-334.

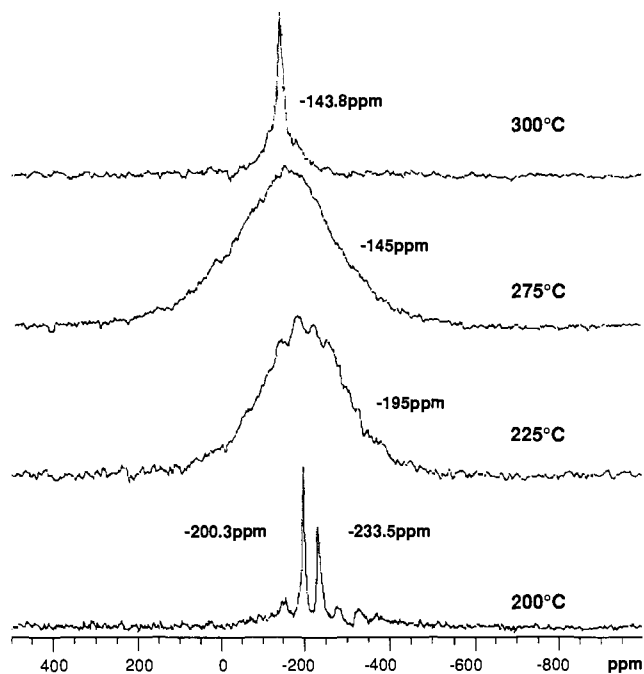


Figure 1. 121.65 MHz ³¹P MAS NMR of microdisperse GaP in zeolite NaY. The numerals indicate the different temperatures of PH₃ treatment of the (Me)_{3-x}Ga loaded samples. All samples contain comparable amounts of phosphorus. Chemical shifts (in ppm, vs 85% H₃PO₄) are indicated in the figure. For the broad signals, the center of gravity is calculated from the first moment. Minor unlabeled peaks represent spinning sidebands.

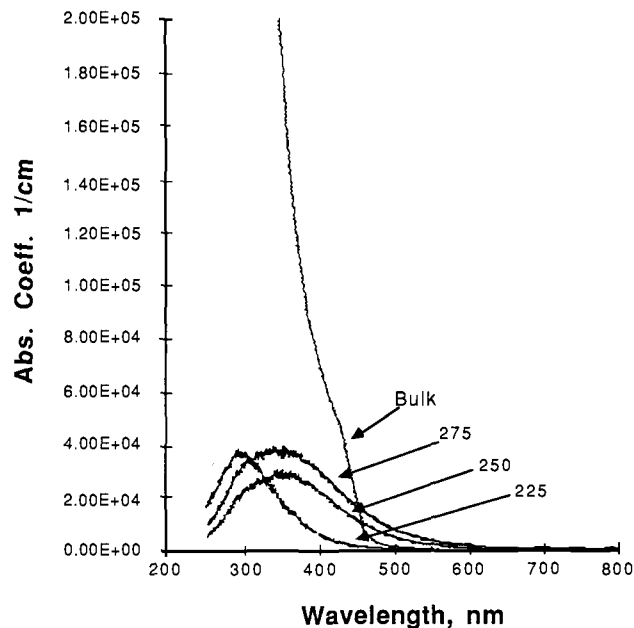


Figure 2. UV-vis spectra of bulk GaP and GaP included in zeolite NaY, treated at 225, 250, and 275 °C in PH₃.

pumped off at room temperature, and the (Me)_{3-x}Ga loaded zeolite is treated with an excess of PH₃ for several hours at a series of temperatures between room temperature and 400 °C. The product is cooled in vacuum and handled in an inert atmosphere thereafter. The color of samples vary with treatment temperature (white below 200 °C and yellow to orange between 200 and 300 °C), and this change is reflected in the systematic trend seen in the UV-vis spectra. Optical spectra in Figure 2 show a pronounced peak at 290 nm for the low-temperature sample and at 350 nm for the high-temperature samples. These absorption peaks are blue shifted from the band gap of bulk GaP (direct 466 nm, indirect 546 nm). We also note that the 250 °C and 275 °C samples absorb to the red of bulk GaP. This may be due to the